

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-349871
 (43)Date of publication of application : 21.12.1999

(51)Int.CI. C09D 11/00

(21)Application number : 10-179551
 (22)Date of filing : 22.05.1998

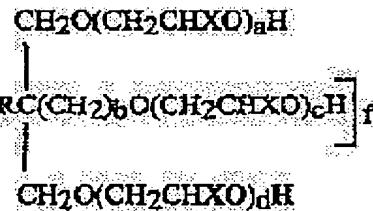
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(54) INK COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an ink compsn. improved in stability, viscosity, optical density, and printing characteristics by compounding an insoluble pigment, a polymeric dispersant for the pigment, an aq. carrier, and an auxiliary solvent mixture comprising specific substances.

SOLUTION: This compsn. comprises (A) ingredients comprising about 0.01–20.0% insoluble pigment, about 0.001–40.0% polymeric dispersant, and about 40.0–99.0% aq. carrier and (B) an auxiliary solvent mixture comprising (a) a 2–8C alkanediol or a mixture thereof and (b) a substance (substances) selected from among (i) polyethylene glycol or a mixture thereof with polypropylene glycol, (ii) a polyol/alkylene oxide condensation product of the formula, and (iii) a mixture of substances (i) and (ii). The wt. ratio of A/B is (about 95/about 5)–(about 5/about 95). In the formula, X is H or a 1–6C alkyl; R is H; a 1–6C alkyl, or $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_e\text{H}$; b is 0 or 1; a+d+f (c+e) is about 2–100; and f is about 1–6.



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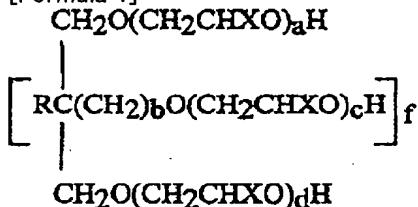
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CLAIMS

[Claim(s)]

[Claim 1] (a) About 0.1 % of the weight – about 20.0% of the weight of coloring agent;
(b) About 0.001 % of the weight – about 40.0% of the weight of polymer dispersant for the above-mentioned coloring agents;
(c) matter; chosen from the group which consists of about 40.0 % of the weight – about 99.0% of the weight of an aquosity carrier; and (d) (1) C2–C8 end alkane diol or such mixture; and (2) following (i) – (iii) — containing — concerned weight ratio [of (1) and (2)] (1): (2) — about 95:5— auxiliary solvent mixture [about 1.0 % of the weight – about 75.0% of the weight of]; which is about 5:95
****, the water–color–ink constituent suitable for use of an ink jet printer.
(i) It is the mixture of a polyethylene glycol and a polypropylene glycol to the polyethylene glycol and row which have about 200 – about 5,000 molecular weight.;
(ii) Condensation product of a polyol / oxidization polyalkylene which has the following formula;

[Formula 1]



here — X — H or C1–C6 alkyl, and R — H, C1–C6 alkyl, or $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})$ — eH, b0 or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1— such (iii) mixture which is about 6

[Claim 2] The ink constituent containing the matter chosen from the group which the aforementioned auxiliary solvent mixture becomes from (1) C2–C8 end alkane diols or such mixture; and (2) following (i) – (iii) according to claim 1.

(i) Polyethylene glycol which has about 200 – about 5,000 molecular weight;
(ii) — the condensation product of a polyol / oxidization alkylene, and here —; whose a+d+f (c+e) of 0 and f hydrogen and b is [X] 26 at 1 and a row for hydrogen and R
(iii) Such mixture.

[Claim 3] The ink constituent containing about 1.0% – about 75.0% of the aforementioned auxiliary solvent mixture according to claim 2.

[Claim 4] The ink constituent according to claim 3 which is the polyethylene glycol in which the aforementioned polyethylene–glycol component (i) has about 200 – about 1,000 molecular weight in the aforementioned auxiliary solvent mixture.

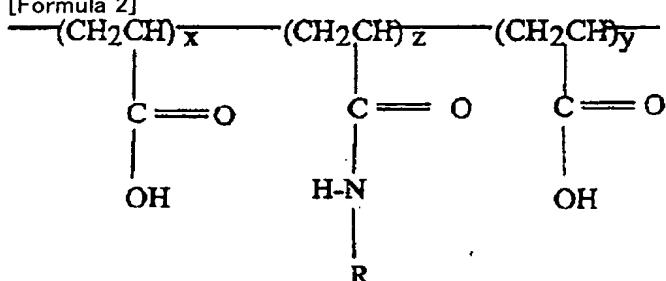
[Claim 5] The ink constituent according to claim 4 whose aforementioned auxiliary solvent mixture is the mixture of 1 and 3–propanediol and the polyethylene glycol which has about 200 – about 1,000 molecular weight.

[Claim 6] The above (1) and the ink constituent according to claim 4 whose weight ratio [of (2)] (1): (2) is about 40:60–60:40.

[Claim 7] The ink constituent according to claim 1 chosen from the group which the aforementioned polymer dispersant becomes from following (a) – (d).

(a)

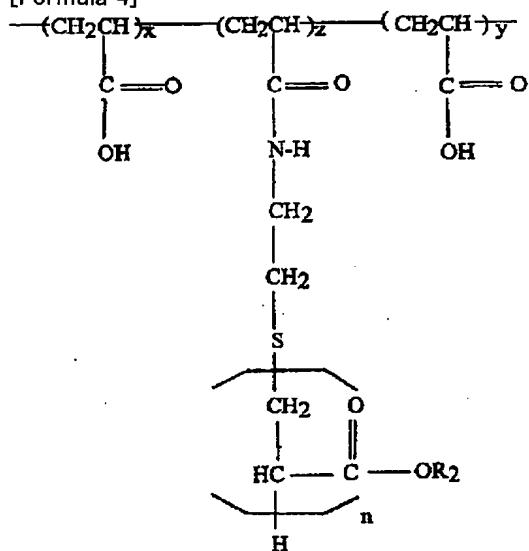
[Formula 2]



here — x+y — about 20 — about 200 z — about 1 — about 10 and RC6 — C36 alkyl — or [Formula 3]
 $R_1 - \text{C}_6\text{H}_4 -$

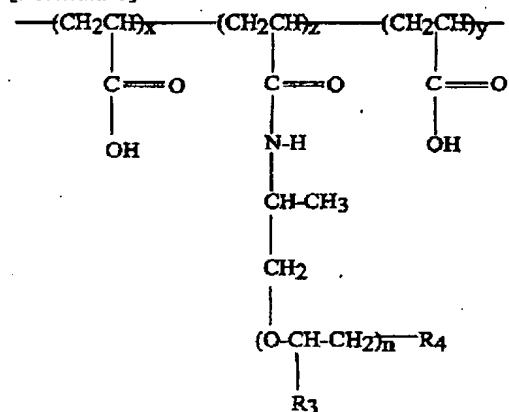
R1 is C4 — C20 alkyl here (b).

[Formula 4]



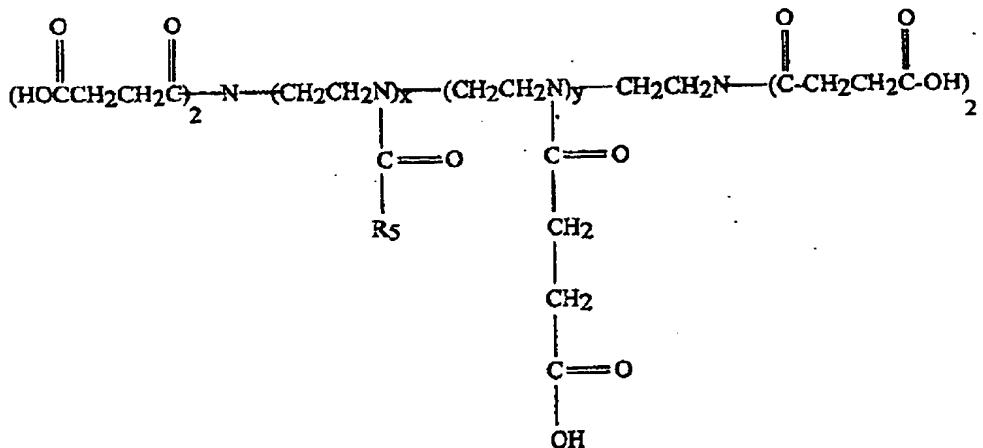
Here, for x+y, about 20 — about 200 z of about 1 — about 10 (it distributed at random) n are [about 2 — abbreviation 40 and R2] an alkyl or an aryl (c).

[Formula 5]



here — x+y — about 20 — about 200 z — about 1 — about 10 (it distributed at random) and R3 — H, or CH3 and R4 — H, CH3, or OCH3 and n — about 10 — it is about 60 (d)

[Formula 6]



Here, y of about 6 – Abbreviation 20 and x is [about 1 – abbreviation 5, and R5] the alkyls of C6-C30.

[Claim 8] The aforementioned aquosity carrier Water; or ethylene glycol, 1 and 2, 6-hexane triol, A thioglycol, a hexylene glycol, a diethylene glycol, Pentanediol, hexandiol, a lauric-acid propylene glycol, A glycerol, an ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, A diethylene-glycol methyl ether, diethylene-glycol ethyl ether, The triethylene-glycol monomethyl ether, the triethylene-glycol monoethyl ether, The ink constituent according to claim 7 which is mixture [of the organic solvent and water which are chosen from the group which consists of a methanol, ethanol, propanol, a butanol, an acetone, a tetrahydrofuran, a dioxane, ethyl acetate, a sulfolane, lactone, lactams, and such mixture].

[Claim 9] The ink constituent according to claim 8 which is the pigment chosen from the group which the aforementioned coloring agent becomes from carbon black, a titanium dioxide, and an iron oxide.

[Claim 10] The ink constituent containing about 0.5% – about 5.0% of the aforementioned coloring agent according to claim 9.

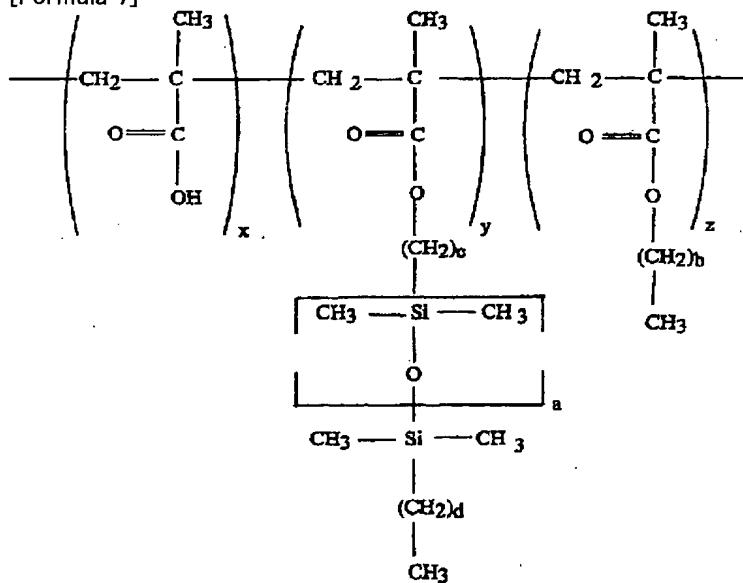
[Claim 11] It has the molecular weight to which the aforementioned polymer dispersant exceeds about 600 – abbreviation 20,000, and is (a) hydrophilic-property polymer segment;:

(b) Stabilization segment which has hydrophobic polymer segment; which has about 400 – about 3,000 molecular weight, and has a stable siloxyl substituent to hydrolysis, and (c) about 200 to about 2,000 molecular weight, and is chosen from the group which consists of reactive-surface-active-agent macromere, protective colloid macromere, and a non-siloxyl hydrophobic monomer;

The ink constituent according to claim 9 which is a graft copolymer containing **.

[Claim 12] The ink constituent according to claim 11 with which the aforementioned polymer dispersant contains the following formula.

[Formula 7]



here -- x -- about 5 – about 100 y -- about 1 – about 2 z -- about 1 – about 5 a -- about 3 – about 45 b -- about 3 – about 29 c -- about two to 8 d -- 0- it is about 7

[Claim 13] The ink constituent containing the matter chosen from the group which the aforementioned auxiliary solvent mixture becomes from (1) C2-C8 end alkane diols or such mixture; and (2) following (i) – (iii) according to claim 11.

(i) Polyethylene glycol which has about 200 – about 5,000 molecular weight;

(ii) For hydrogen and R, X is [hydrogen and b / 0 and f] such (iii) mixture whose a+d+f (c+e) is 26 at 1 and a row the condensation product of a polyol / oxidization alkylene, and here.

[Claim 14] The ink constituent containing about 1.0% – about 75.0% of the aforementioned auxiliary solvent mixture according to claim 13.

[Claim 15] The ink constituent containing the matter chosen from the group which the aforementioned auxiliary solvent mixture becomes from (1) 1, 3-propanediol, 1, 4-butanediol, 1,5-pentanediol, 1, and 6-pentanediol or such mixture; and (2) following (i) – (iii) according to claim 14.

(i) Polyethylene glycol which has about 400 molecular weight;

(ii) For hydrogen and R, X is [hydrogen and b / 0 and f] such (iii) mixture whose a+d+f (c+e) is 26 at 1 and a row the condensation product of a polyol / oxidization alkylene, and here.

[Claim 16] The above (1) and the ink constituent according to claim 15 whose weight ratio [of (2)] (1): (2) is about 40:60.

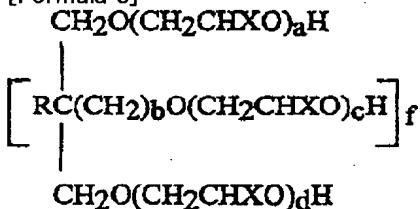
[Claim 17] The ink constituent according to claim 16 with which the aforementioned aquosity carrier is mixture [of the organic solvent and water which are chosen from the group which consists of water; or a glycerol, a thiodiglycol, n-propanol, and such mixture], and contains about 50% of the weight of water / water of about 50% of the weight of an organic solvent – 99.9 % of the weight of abbreviation / about 0.1% of the weight of organic solvent.

[Claim 18] (1) Auxiliary solvent mixture containing the matter chosen from the group which consists of C2-C8 end alkane diols or such mixture; and (2) following (i) – (iii).

(i) It is the mixture of a polyethylene glycol and a polypropylene glycol to the polyethylene glycol and row which have about 200 – about 5,000 molecular weight;

(ii) Condensation product of a polyol / oxidization polyalkylene which has the following formula;

[Formula 8]



here — X — H or C1-C6 alkyl, and R — H, C1-C6 alkyl, or $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})$ — eH, b0 or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1– such (iii) mixture which is about 6

[Claim 19] Auxiliary solvent mixture according to claim 18 whose aforementioned end alkane diols are 1, 3-propanediol, 1, 4-butanediol, 1,5-pentanediol, 1, and 6-pentanediol or such mixture.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the ink constituent used for an ink jet printer.

[0002]

[Description of the Prior Art] Ink-jet printing is performed by injecting ink from a nozzle to paper or other print media. Ink can be made to inject by various kinds of methods towards a medium. For example, in electrostatic printing, ink is injected by the electrostatic field towards a medium from a nozzle. In the procedure of other ink-jet printings known as a squeeze tube, the piezoelectric device is used into an ink nozzle. Ink is transported to print media through a nozzle by the electric distortion of a piezoelectric device. In the procedure of other ink-jet printings in which thermal ** is known as bubble ink-jet printing, when the bubble of a gaseous phase expands within a nozzle, ink is injected towards print media from a nozzle. The print processes of these various kinds are indicated by issue (refer to Chapter 13 "ink-jet printing" especially) in DABEKU and edited by Shache "hard copy output unit", and Academic Press 1988.

[0003] The ink constituent used for an ink jet printer usually contains the organic solvent of deionized water, water solubility, or water and compatibility, and a coloring agent. Generally, a coloring agent is the color of fusibility. A low and chemicals-proof nature have [the thermal stability whose printing quality is not good] many problems of a low, being easy to oxidize in the ink [it is regrettable and] which contains a fusibility color especially including bleeding, feathering, etc. of ink which plugging produces in an injection channel by the evaporation of a solvent which is not [a low and lightfastness] good, or change of the solubility of a color and which a color crystallizes.

[0004] Many of these problems are solvable by using an insoluble pigment instead of the fusibility color used for ink prescription. Generally, the pigment is excellent in the property as compared with the color, and excellent in respect of the ability to also suit especially water resistance, lightfastness, thermal stability, oxidation stability, and the paper coated or processed also at a regular paper. However, in order not to dissolve in an ink constituent, therefore to make it distribute, some new problems produce a pigment. The stability of ink is very important for maintaining the homogeneity of a property, and a row in the point of making it both not get a pigment blocked in an ink jet, while not using it. It is ideal to make the amount of a pigment required in an ink constituent, of course into the minimum from the reason of both stability and cost. However, if the amount of the pigment in an ink constituent is reduced, the optical density of a picture will fall. Furthermore, in order to secure required stability, while the balance of composition is required, therefore has suitable viscosity in an ink jet printer using a constituent, when it prints on paper, it is important [water resistance and lightfastness are good, and] that running and feathering are also the minimum. It was very difficult to develop ink prescription which optimized all of these properties until now. Adjusting the dispersant and solvent system of an ink constituent for the purpose of maintaining and optimizing the balance of these properties that conflict in many cases as common practice was performed. However, prescription which optimized all these properties, without using a specific polymer dispersant before this invention was not attained.

[0005] The ink constituent for ink jets which contains the auxiliary solvent of a water carrier medium, pigment dispersion liquid, and a polyol and an oxidization alkylene in the U.S. Pat. No. 5,180,425 specification of the matric on January 19, 1993 is indicated. The life of ink jet printer ability is lengthened and these ink is taught that there is coat-proof formation nature. RAIPo nick EG-1 is one of the indicated desirable auxiliary solvents. The polyethylene glycol is contained in other solvents used for this patent.

[0006] Pigment dispersion liquid, the water carrier medium, and a polyol, the condensation product of an oxidization alkylene and the ink constituent containing the auxiliary solvent mixture containing a cyclic-amide derivative for ink jets are indicated by the U.S. Pat. No. 5,302,197 specification of wick Lamasma NAIKE on April 12, 1994. It is taught that RAIPo nick EG-1 is useful as a condensation-product component of a polyol and an oxidization alkylene.

[0007] An aquosity carrier medium, a specific alkyl polyol ether auxiliary solvent, and the ink for ink jets that consists of pigment dispersion liquid (what stabilized the pigment particle with the dispersant) are indicated by the Europe patent No. 603,469 application of Chillan and others on June 29, 1994. It is taught that these ink has viscosity, surface tension, plugging prevention of a nozzle, printing quality, light stability, bleeding-proof nature, and waterproof good balance. 1, 2, and 3-butane triol is contained in the solvent used by invention of an indication.

[0008] A clear image is formed in the U.S. Pat. No. 4,597,794 specification of OTA and others on July 1, 1986, and ink prescription used for the ink-jet printing process said to have a good physical property is indicated. A polyethylene glycol and 1, 2, and 6-hexane triol are contained in the solvent indicated especially in order to use it

for this ink.

[0009] Giving characteristic mixture, when optimizing a property was found out by using the specific auxiliary solvent mixture which contains C2-C8 end alkane diols or such mixture with either the polyethylene glycol of (a) low molecular weight, a related compound or the condensation product of the (b) polyol and an oxidization alkylene for the water-color-ink constituent containing the dispersion liquid of an insoluble pigment. Especially, the property these constituents excelled [property] in stability, optical density, viscosity, the printing property (running of feathering in water resistance and the printed page and ink is the minimum), and the row in points, such as a problem (the blinding of the printer jet at the time of printer un-using it is the minimum) of printer maintenance, (even when low pigment concentration is used) is acquired. About the combination of the specific auxiliary solvent shown by this invention, neither a publication nor suggestion has each in the above-mentioned patent.

[0010]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the pigment ink constituent with which it has been improved for [containing a specific auxiliary solvent system] ink jet printers.

[0011]

[Means for Solving the Problem] Other purposes and features of this invention become clear by the following indication.

[0012] this invention is the insoluble pigment of 0.01% – about 20.0% of (a) abbreviation.:

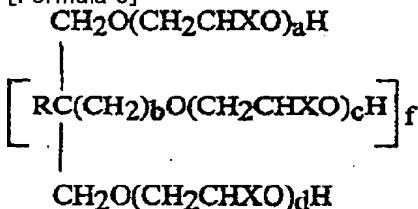
(b) About 0.001% – about 40.0% of polymer dispersant for the aforementioned pigments;

(c) It is related with the water-color-ink constituent containing about 1.0% – about 75.0% of auxiliary solvent mixture containing about 40.0% – about 99.0% of aquosity carrier; and (d) (1) C2-C8 end alkane diols or such mixture, and the matter chosen from the group which consists of (2) following (i) – (iii) suitable for use of an ink jet printer.

(i) Condensation product of a polyol / oxidization alkylene which has about 200 – about 5,000 molecular weight and which has the mixture of a polyethylene glycol and a polypropylene glycol, and the formula of (ii) following in a polyethylene glycol and a row.

[0013]

[Formula 9]



[0014] here — X — H or C1 – C6 alkyl, and R — H, C1 – C6 alkyl, or $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})$ — eH, b0 or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1 – it is about 6

(iii) Such mixture.

In addition, above-mentioned (1) ratio [of : (2) / weight] (1): (2) is about 95:5 – abbreviation 5:95.

[0015] The percentage and the ratios which were used for this specification are "weight %" and a "weight ratio", unless it otherwise specifies. The molecular weight used for this specification is number average molecular weight, unless it otherwise specifies. A C2-C8 end alkane diol is defined as each end as what means the diol which has a hydroxy group, for example, the alkane diol which has the following formula.

[0016]

[Formula 10]



Here, t is about 0 – abbreviation 6.

[0017]

[Embodiments of the Invention] this invention relates to the water-color-ink constituent suitable for using it for an ink jet printer. These constituents contain the polymer dispersant (a pigment and a dispersant exist in the constituent as dispersion liquid), the aquosity carrier, and the specific auxiliary solvent mixture for a coloring agent (for example, carbon black, cyanogen, a Magenta, or a yellow pigment) like an insoluble pigment, and a pigment. Each of these required components is explained in detail below with some additional components.

[0018] a polymer dispersant — the constituent of this invention — setting — about 0.001% – about 40.0% of the last component — it is contained about 0.5% to about 5.0% most preferably about 0.25% to about 10.0% both the anion nature by which it is known for the industry that it is suitable for using it for the polymer dispersant suitable for using it by this invention as a dispersant of the ink manufacture object for ink jets cation nature and a non-ionicity polymer — although — it is contained The example of such a material is indicated by the U.S. Pat. No. 5,310,778 specification of Shore and others on May 10, 1994 appended to this specification as reference. A homopolymer, a copolymer, the letter polymer of branching, or a graft polymer is sufficient as such a polymer dispersant. Moreover, a random polymer or a block polymer is sufficient.

[0019] The block copolymer of AB, BAB, and ABC is one sort of a polymer dispersant useful to this invention.

Desirable things are AB and BAB which were guided from at least one sort of alkyl acrylics or a methacrylic ester and an amine substitution acrylic, or the monomers of a methacrylic ester, and an ABC block copolymer. Desirable

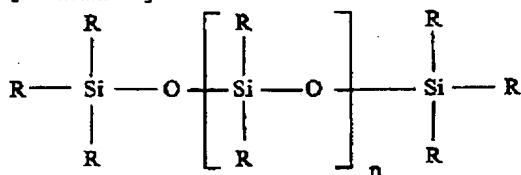
AB and BAB block copolymers, and these processes are indicated by the U.S. Pat. No. 5,085,698 specification of MA and others on February 4, 1992 appended to this specification as reference.

[0020] A polymer dispersant useful to operation of this invention usually tends to combine a hydrophobic segment with the pigment particle in an ink constituent including both polymer segments of a hydrophobic property and a hydrophilic property, it is tended by the liquid ink medium to carry out the solvation of the hydrophilic segment, and it stabilizes dispersion liquid according to these, a three-dimensional mechanism, and/or an ionicity mechanism.

[0021] The desirable polymer dispersant of a kind used by this invention contains the block or graft copolymer containing a hydrophilic polymer segment and the hydrophobic polymer segment which contains a stable siloxyl substituent to hydrolysis. Especially a desirable thing is a graft copolymer containing a hydrophilic polymer segment (especially acrylate or a methacrylate copolymer) and the hydrophobic polymer segment guided from the macromere which has the following formula among the groups of these dispersants.

[0022]

[Formula 11]



[0023] n is the low-grade alkyl (C1-C6) or siloxyl which 2-16R became independent of, respectively among a formula. Such material is indicated by the U.S. patent application 08th/No. 360,199 specification of December 21, 1994 and beaches appended to this specification as reference.

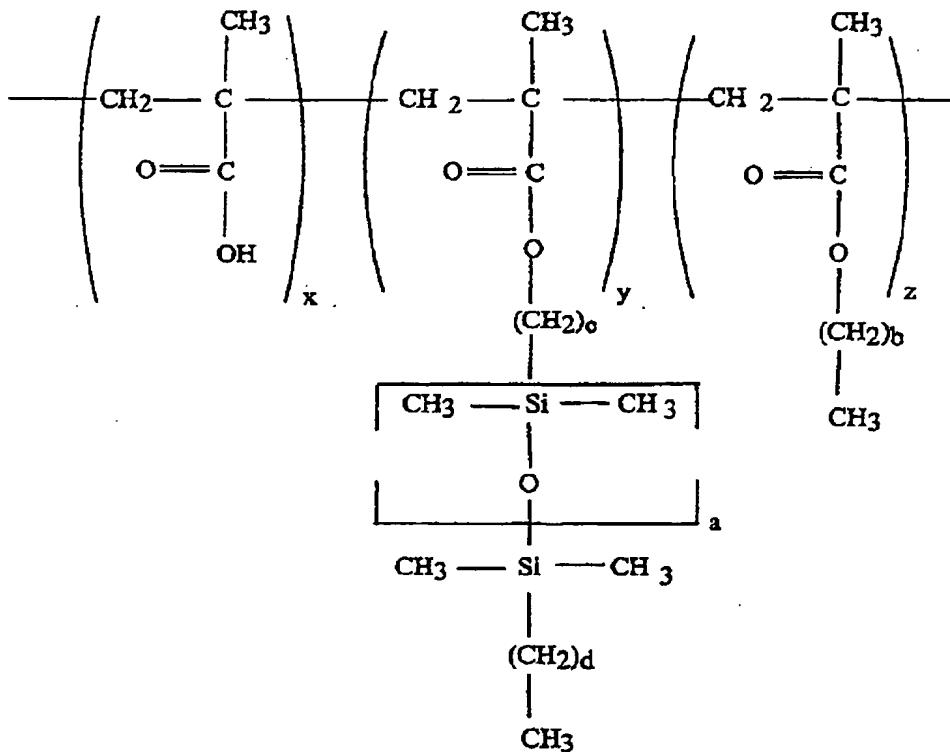
[0024] The desirable polymerization nature powder of other kinds is a graft copolymer containing the hydrophobic polymer segment which has about 600 - about 20,000 molecular weight, has a stable siloxyl substituent to (a) hydrophilic-property polymer segment and (b) hydrolysis, and has about 400 - about 3,000 molecular weight, and the stabilization segment chosen from the group which becomes a row from the surface activity macromere of (c) reactivity, protective colloid macromere, and a non-siloxyl hydrophobic monomer.

[0025] Desirable monomer ratio (a) : (b) is about 10:1 - abbreviation 100:1, and ratio [of a desirable monomer] (b): (c) is about 2:1 - abbreviation 1:5. A desirable hydrophilic polymer segment has a bitter taste relay torr or the most desirable meta-chestnut rhe torr polymer matter including a carboxy substituent. A desirable siloxane content hydrophobic polymer segment is macromere of the poly dialkyl siloxane which has an acryloyl or a methacryloyl machine at the end. The most desirable hydrophobic segment is ** which has about 400 - about 2,000 molecular weight, and has a dimethyl polysiloxyl machine. A desirable stabilization segment Stearylacrylate, stearyl methacrylate, Laurylacrylate, lauryl methacrylate, nonyl-phenol acrylate, Nonyl-phenol methacrylate, n - about 1-nonyl phenoxy poly (ethyleneoxy) n methacrylate which is about 40; n - about 1- nonyl phenoxy poly (ethyleneoxy) n acrylate which is about 40; n - about 5- methoxy poly (ethyleneoxy) n methacrylate which is about 40; Methoxy poly whose n is about 5 - abbreviation 40 (Ethyleneoxy) n acrylate; Stearyl oxy-poly whose n is about 1 - abbreviation 20 (Ethyleneoxy) n methacrylate; Stearyl oxy-poly whose n is about 1 - abbreviation 20 (Ethyleneoxy) n acrylate; - fluorine-ized C1-C18 alkyl methacrylate; - fluorine-ized C1-C18 alkyl acrylate; - poly (propylene glycol) methyl-ether methacrylate; - poly (propylene glycol) methyl-ether acrylate - Poly (Propylene glycol) 4-nonylphenyl ether methacrylate; - poly (propylene glycol) 4-nonylphenyl ether acrylate; - polyethylene-oxide; which has a metacryloxy machine and a trimethylsiloxy machine at the end - Polyethylene-oxide; which has an acrylic oxy-basis and a trimethylsiloxy machine, and such mixture are included in an end.

[0026] The most desirable thing has the following formula in a principal chain with this kind of polymer dispersant.

[0027]

[Formula 12]

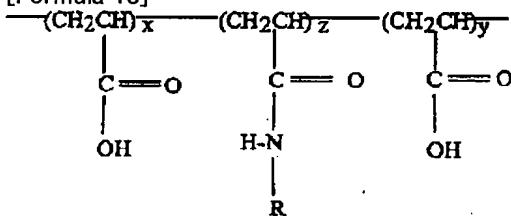


[0028] The inside of a formula, 3; x — about 5— about 100 — desirable — about 15 — about 50 y — about 1— about 2 — desirable — about 1 z — about 1— about 5 — desirable — about 1 —;a — about 3— about 45 — desirable — about 9 b — about 3— about 29 — desirable — about 15 — about 17 c — about 2— about 8 — desirable — about — d — 0— about 7 — it is about 3 preferably These polymer dispersants are indicated by the U.S. patent application "the polymer dispersant for pigment use ink" of ***** of the beaches appended to this specification as reference. The end group of the dispersant of this invention is not limited. For the purpose of explanation, it is contained like [a thio substitution hydrocarbon] hydrogen.

[0029] The polymer dispersant of other kinds is indicated by the U.S. patent application 08th/No. 360,200 specification of December 21, 1994 and beaches appended to this specification as reference. These matter is the graft polymers containing the hydrophobic segment side chain which has one side chain combined with one principal chain as preferably as the principal chain of the hydrophilic polyacrylic acid of the weight average molecular weight of about 1,000 — about 5,000 between. This kind of desirable polymer has one of the following structure expressions.

[0030]

[Formula 13]



[0031] the inside of a formula, and x+y — about 20 — about 200 z — about 1 — about 10 R — the alkyl of C6-C36 — — or [0032]

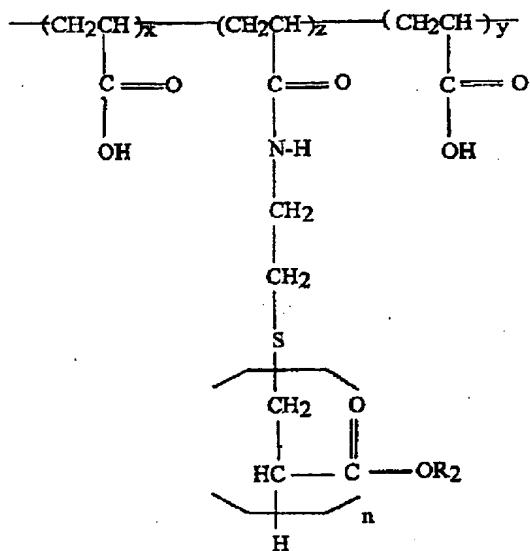
[Formula 14]



R₁ is the alkyl or the following basis of C4-C20 here.

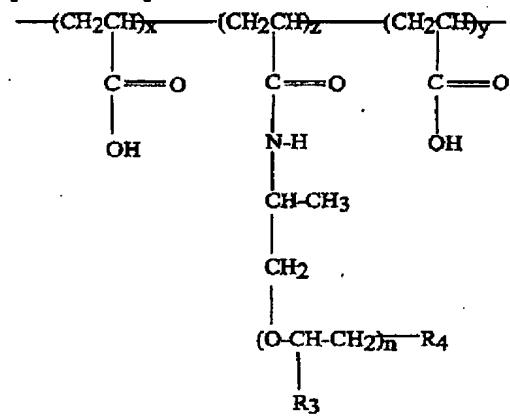
[0033]

[Formula 15]



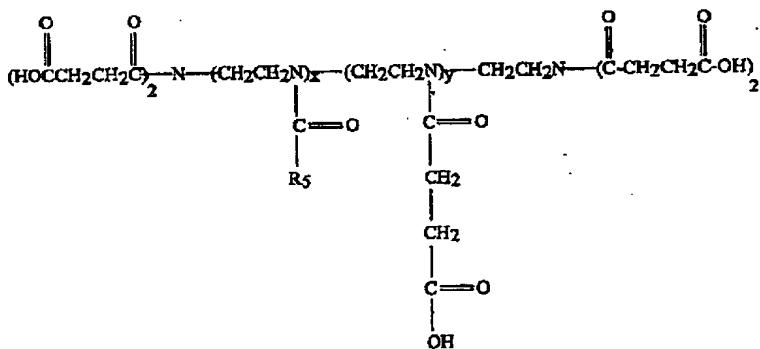
[0034] the inside of a formula, and $x+y$ — about 20 — about 200 z — about 1 — about 10 (it distributed at random) n — about 2 — about 40 and R_2 — an alkyl or an aryl — desirable — butyl — or [0035]

[Formula 16]



[0036] the inside of a formula, and $x+y$ — about 20 — about 200 z — about 1 — about 10 and R_3 — H, or CH₃ and R_4 — H, CH₃, or OCH₃ and n — about 10 — about 60 — or [0037]

[Formula 17]



[0038] y of about 6 — Abbreviation 20 and x is [about 1 — abbreviation 5, and R_5] the alkyls of C₆—C₃₀ among a formula.

[0039] The graft copolymer dispersant of this invention is low molecular weight comparatively, in order to acquire the stability of a particle, and its viscosity needs to be low in order to use it for the stable ink for ink-jet printing. For this reason, the polar-solvent polymerization method for generating a copolymer is chosen. The molecular weight of a copolymer and homogeneity are controlled by such method by maintaining the solubility of not only the copolymer obtained but all start raw materials (it is a chain transfer agent to a free radical initiator, a hydrophobic

property and a hydrophilic monomer, and a row). In order to write a prescription to ink-jet printing and to make a water medium suspend the compounded copolymer, it needs to collect copolymers from the polar organic solvent in reaction mixture, and it is necessary to make it dissolve them in water. The copolymer recovery method from a typical polar polymerization solvent includes the following processes.

1. The solution of a copolymer is added to non-solvents, such as a hexane, a polymer is settled from a solution, this refines a copolymer, vacuum filtration of the 2. precipitate is carried out, and 3. copolymer precipitate is dried.

[0040] Next, copolymer powder can be dissolved in a water base and it can be used for generation of the ink for ink-jet printing. This method has high cost and is superfluously complicated. [of cost]

[0041] The desirable method for collecting the dispersants of a copolymer from a polar organic polymerization solvent improves printing quality which decreases it not only merely collects the dispersants of a copolymer, but that the ink-jet ink generated from these dispersants forms a satellite and a splatter. Specifically, these desirable methods include the following process.

1. Dissolve in a water base and exchange 2. solvent, after evaporating a solvent.

[0042] At solvent evaporation and a dissolution process, vacuum tray dryness, rotation evaporation dryness, drum dryness, a turning-circle cylinder vacuum drying, or spray drying evaporates a polar solvent from a copolymer first by the standard method of changing the solution of a copolymer into dryness powder. Next, the dry copolymer powder is dissolved in a water base, and it enables it to use it for generation of the ink of the pigment for ink jets.

[0043] a solvent exchange-buffering-method process — about 35% — about 60% of the polar solvent in a polymerization reactor (preferably about 50%) — distillation — removing — deionized water and a water base (for example, KOH solution) — adding — pH — about 4.5— about 6.5 — it adjusts to about 5 preferably In the case of a polar solvent with the boiling point lower than water, in order to make a solvent distill, the temperature of this mixture is slowly raised, until temperature amounts to about 100 degrees C from which all polar solvents are removed. (This process cannot be used when the boiling point of a polar solvent is higher than the boiling point of water.) further — a water base (for example, KOH solution) — this solution — in addition, pH — about 7— about 8.5 — about 7.5 is raised preferably Subsequently, this solution is used for prescription of the pigment ink for ink jets.

[0044] The 2nd component of the ink constituent of this invention is a pigment which is an insoluble coloring agent. the constituent of this invention — a pigment — the last constituent — receiving — about 0.1% — about 20.0% — about 0.5% — 5.0% exists most preferably about 0.25% to about 10.0% Actually, one of the important advantages of this invention enables prescription of ink which has low pigment concentration (for example, for 0.5% — 5.0%), and moreover, it is quality and is offering the outstanding optical density. All of the well-known conventional pigment can be used in this industry that is indicated as a pigment useful to operation of this invention by the U.S. Pat. No. 5,085,698 specification of February 4, 1992, MA and others appended to this specification as reference. Even if it uses it independently, you may use a pigment, combining.

[0045] The particle of a pigment needs to have [an ink-jet printer, especially a diameter] small ink enough so that the inside of the injection nozzle which is usually about 10 micrometers — about 100 micrometers can be flowed freely. Particle size affects the distributed stability of an important pigment through the life of ink again. The Brownian motion of a particle is useful to condensation prevention of a particle, and, thereby, a product is stabilized further. In order to make color intensity and gloss into the maximum, it is also desirable to use a small particle. A useful size range is about 0.05 microns — about 15 microns. The range of the particle size of a pigment is about 0.05 microns — about 5 microns, and the range of it is about 0.05 microns — about 1 micron most preferably. A pigment can be used also with the gestalt which carried out [the dry gestalt or] humidity. For example, a pigment is usually manufactured in an aquosity medium and is obtained as a filter press cake containing water. With the gestalt of this filter press cake, a pigment is not condensed like [in the case of a dryness gestalt]. Therefore, the pigment of the gestalt of the filter press cake containing water does not need to perform solution condensation in the manufacturing process of ink like [at the time of using the dry pigment].

[0046] The particle of a metal or a metallic oxide can also be used for operation of this invention. For example, the metal and the metallic oxide are suitable for manufacture of the ink for magnetic ink jets. The oxide of a particle, for example, a silica, an alumina, a titania, etc. can be used. Furthermore, the pulverized metal particles, for example, copper, iron, steel, aluminum, and alloys can be chosen because of a suitable use.

[0047] there are inorganic pigments, such as organic pigment; titanium oxide, such as color lake; nitroglycerine pigments, such as polycyclic formula pigment; basic dye lakes, such as azo pigment; phthalocyanine pigments, such as an azo lake, insoluble azo pigment, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, an anthraquinone pigment, a Quinacridone pigment, a dioxazine pigment, a thio indigo pigment, an isoindolinone pigment, and a kino FUTARON pigment, and an acid-dye lake, an oximido pigment, an aniline black, and a daylight fluorescent pigment, an iron oxide, and carbon black, etc. in A desirable pigment contains titanium oxide, an iron oxide, and carbon black in using it in this invention. For the example of the available pigment of marketing which can be used in this invention Brand name Heliogen Blue L 6901F (BASF), Brand name Heliogen Blue NBD 7010 (BASF), Brand name Heliogen Blue K7090 (BASF), brand name Heucophthal Blue GXBT-583D (HYU back), Brand name Irgalite Rubin 4BL (Ciba-Geigy), Brand name Quindo A Magenta (Mobey), a brand-name Indofast brilliant scarlet (Mobey), Brand name Hostaperm Scarlett GO (Hoechst), Permanent Rubin F6B (Hoechst), brand name Monastral Scarlett (Ciba-Geigy), A brand name Raven1170 (COL KEMU), SUPESSHARU black 4A (Degussa AG), Black FW18 (Degussa AG), brand name Sterling NS Black (Cabot), Brand name Sterling NSX 76 (Cabot) Monarch880 (Cabot), Brand name Tipure R-101 (E. I. du Pont de Nemours), MOGARUL (Cabot) BK 8200 (pole URITCHI) Brand name Heliogen Green K 8683 (BASF), Brand name Heliogen Green L9140 (BASF), Brand name Monastral Red B (Ciba-

Geigy), brand name Monastral Violet R (Ciba-Geigy) Brand name Hostaperm Orange GR (Hoechst), brand name Paliogen Orange (BASF), L75-2377 Yellow (Sun KEMU) and L74-1357 Yellow (Sun KEMU), Brand-name Hostaperm yellow H4G (Hoechst), brand name Argazin Yellow 5GT (Ciba-Geigy), Permanent Yellow G3 R-01 (Hoechst), brand name Novoperm Yellow FGL (Hoechst), Brand name Chromophthal Yellow 3G (Ciba-Geigy), HANZA Yellow X (Hoechst), brand name Dalamar Yellow YT-858-D (HYU back), HANZA — brilliant Yellow SANFASUTO 15:4 (Sun Chemical) etc. is in 5GX-02 (Hoechst), SANFASUTO 15:3 (Sun Chemical), and a row.

[0048] The 3rd component of the ink constituent of this invention is an aquosity carrier medium. This component is the mixture of water (preferably deionized water) or water, and at least one kind of water-soluble organic solvent. an aquosity carrier component — constituent [of this invention / about 40.0% of] — about 98.99 — about 50.0% — about 80.0% exists preferably Selection of suitable mixture is dependent on the kind of paper in which ink is printed by the drying time required for the requirements for the specific ink prescribed, for example, desirable surface tension, viscosity, the pigment to be used, and pigment ink, and the row etc. As an example of representation of the water-soluble organic solvent which can be chosen (1) Methyl alcohol, ethyl alcohol, n-propyl alcohol, Isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, furfuryl alcohol, Alcohols; (2) acetones, such as a tetrahydrofurfuryl alcohol, Ketones or keto-alcohols; (3) tetrahydrofurans, such as a methyl ethyl ketone and diacetone alcohol, Ether; (4) ethyl acetate, such as a dioxane, an ethyl lactate, an ethylene carbonate, Ester; (5) diethylene glycols, such as a propylene carbonate, a glycerol, The 2-methyl -2, 4-pentanediol, 1 and 2, 6-hexane triol, Polyhydric alcohol, such as a thiodiglycol; (6) ethylene-glycol monomethyl (or monoethyl) ether, The diethylene-glycol monomethyl (or monoethyl) ether, the propylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl monochrome guided from alkylene glycol, such as the triethylene-glycol monomethyl (or monoethyl) ether and the diethylene-glycol dimethyl (or diethyl) ether, or a diethers; (7) pyrrolidone, a N-methyl-2-pyrrolidone, There are sulfur content compounds, such as nitrogen content cyclic compounds, such as 1-(2-hydroxyethyl)-2-pyrrolidone, 1, and 3-dimethyl-2-imidazolidinone, (8) dimethyl sulfoxide, and a tetramethylen sulfone. There are lactone and lactams in other useful solvents.

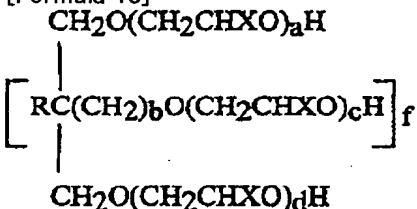
[0049] When using the mixture of water and an organic solvent as a carrier medium by this invention, a medium usually contains about 0.1% of water / water of 99.9% of organic solvent — 99.9% of abbreviation / 0.1% of organic solvent. Desirable ratios are about 50% of water / water of 50% of organic solvent — 90.0% of abbreviation / about 10.0% of organic solvent. Such percentage receives the total weight of a water carrier medium. What is used for a water carrier medium in the term of the "organic solvent" used on these specifications should understand that it is not what means that a specific material used as a component of the auxiliary solvent of this invention is included.

[0050] In the desirable organic solvent used for the water carrier medium component of this invention Ethylene glycol, 1 and 2, 6-hexane triol, a thiodiglycol, Polyhydric alcohol, such as a hexylene glycol and a diethylene glycol; The pentanediol of a non-end (as [give / here / a definition]), Glycol ethers, such as diols; lauric-acid propylene glycols, such as hexandiol and homologous-series diols; Glycerol; and the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl ether of which polyhydric alcohol; A methanol, ethanol, Ketones [such as an alcohols; acetone,], such as propanol and a butanol; A tetrahydrofuran, Ether, such as a dioxane; there are lactams, such as lactone;2-pyrrolidones, such as ester; gamma-butyrolactones, such as ethyl acetate, sulfolanes, and N-methyl pyrrolidone, and a 1-methyl-2-pyrrolidone. Although an organic solvent gives useful properties, such as shortening of the drying time, reduction of bleeding, and increase of permeability, to an ink constituent, generally (the auxiliary solvent matter defined as this specification is a difference), optical density, the stability of a constituent, or printing quality is not improved. A glycerol, a thiodiglycol, n-propanol, and such mixture are in a desirable organic solvent especially.

[0051] The component of the last required to use it with the constituent of this invention is auxiliary solvent mixture, and occupies about 10.0% — about 30.0% most preferably about 5.0% to about 30.0% 1.0% — about 75.0% of abbreviation of the last constituent. This auxiliary solvent mixture contains the C2-C8 end alkane diols which are the first component, or such mixture. Furthermore, the polyethylene-glycol type compound which is the second component, the condensation product of a polyol and an oxidization alkylene, or the mixture of these compounds is also contained. the 2nd component used for this auxiliary solvent mixture — molecular weight — about 200- about 5,000 — it is the mixture of about 200 — about 3,000 polyethylene glycol or a polyethylene glycol, and a polypropylene glycol preferably It is the polyethylene glycol which a polyethylene glycol (PEG) is used most preferably and has about 200 to 1,000 molecular weight preferably. The 2nd component of an auxiliary solvent may be a condensation product of a polyol and an oxidization alkylene which has the following formula.

[0052]

[Formula 18]



[0053] the inside of a formula, and x — H, or CH₃ and R — the alkyl of H, C₁-C₄, or -CH₂O (CH₂CH₂O) — eH, b₀ or 1, and a+d+f (c+e) — about 2 — about 100 f — about 1- it is about 6

[0054] The condensation product of a useful polyol and a useful oxidization alkylene is a resultant of a polyol and an oxidization alkylene in this invention. These are indicated by the U.S. Pat. No. 5,180,425 specification of January 19, 1993 and matric appended to this specification as reference. Solubility [usually as opposed to water in these compounds] is about 4.5% (4.5 sections [as opposed to / the water 100 section / Namely,]) at least at 25 degrees C. The oxidization alkylene used for these compounds is the mixture of an ethyleneoxide, a propylene oxide, or both oxides. Although the mixture of the compound with which the degrees of oxy-alkylation differ is produced by the reaction with a single oxidization alkylene, the shown structure is based on the average composition containing a series of oxidization alkylene units. The random and block copolymer of a propylene oxide and an ethyleneoxide can be used. The oxidization alkylene and the polyol which reacted may have three or more hydroxyl groups. Useful triol is a glycerol, a trimethylol propane, and trimethylolethane. Other triol, such as 1, 2, and 4-butane triol and 1, 2, and 6-hexane triol, can be used. Useful tetrols have a pentaerythritol, JI (trimethylol propane), a methyl glucoside, etc. A glucose, a pen toll, etc. can be used. A sorbitol is useful HEKISORU. Other useful HEKISORU has a JIPENTA erythritol and an inositol. Usually, since such a condensation product is not compatibility, generally it is not suitable for the oxidization alkylene condensation product of a diol to pigment dispersion liquid for using it by this invention. One of the exception of the is a condensation product with the oxidization alkylene of neopentyl glycol.

[0055] There are the following in the example of the condensation product of a polyol and an oxidization alkylene.

[0056]

[Table 1]

表

製品	R	a + d + f		
		(c + e)	b	f
Liponic®EG-1 ¹	-H	26	0	1
Liponic®SO-20 ²	-H	20	0	4
Photonol®PHO-7149 ²	-C ₂ H ₅	2.7	1	1
Photonol®PHO-7155 ²	-C ₂ H ₅	7.4	1	1
Voranol®230-660 ³	-CH ₃	3.0	1	1
Voranol®234-630 ³	-C ₂ H ₅	3.0	1	1
Fomrez®T-279 ⁴	-C ₂ H ₅	3.1	1	1
Fomrez®T-315 ⁴	-C ₂ H ₅	4:1	1	1

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³ダウ・ケミカル・カンパニー、ミッドランド、M. I.

⁴ウイトコ・コーポレーション・オーガニック・デバイジョン、ニューヨーク、

N. Y.

[0057] The condensation product of a polyol and an oxidization alkylene especially desirable although it is used by this invention is above Liponic. It is EG-1. This material has the name of CTFA of GURISERESU-26, is what added the 26-mol ethyleneoxide to the glycerol, and is marketed from a RIPO Chemicals company, Paterson, and New Jersey.

[0058] The first of auxiliary solvent mixture and the second component exist by the weight ratio (the first component : the second component) of about 90:10 - abbreviation 10:90. the weight ratio of a PEG:diol optimal when auxiliary solvent mixture contains a polyethylene-glycol (PEG) type compound and a C₂-C₈ end alkane diol -- about 50:50- it is about 70:30 The condensation product optimal when auxiliary solvent mixture contains the condensation product of a polyol and an oxidization alkylene with C₂-C₈ end alkane diols or such mixture: Diol ratios are about 95:5 - abbreviation 5:95. The ratio of the general most desirable assistant solvent mixture is about 40:60-60:40.

[0059] In order to manufacture such a constituent, you may prepare the ink constituent of this invention by what method learned for this industry. The important point of this constituent is that a pigment and a polymer dispersant form stable dispersion liquid in an aquosity carrier and an auxiliary solvent mixture. By one method both, a polymer dispersant is first mixed with a pigment, next it grinds with a grinding machine, and a particle is decreased to permission particle size. Next, this material is mixed with other ink components. The ink of predetermined concentration is obtained. A surfactant can be added by request, distribution of a pigment can be raised, the surface tension of ink can be changed, and osmosis on paper can be controlled. There are non-ionicity, amphotericism, and an ionic surfactant in a suitable surfactant. In order to acquire the advantage from which other additives, for example, a destruction-of-life agent, the wetting agent, the chelating agent, the viscosity controlling agent, etc. were known for

this industry, it can add to this ink constituent by the operating concentration established in this industry. Generally, in order to promote distribution of a pigment, it is desirable to manufacture Ink-jet, Inc. in the concentration gestalt containing the pigment. Subsequently, it dilutes to suitable concentration to use this ink by the ink jet and the printing system.

[0060] By the method of generating the pigment ink for ink jets, it is required to usually decrease the size of a particle using a trituration mill. The particle size of a pigment needs that less than about 200nm of demands of the self-stable life of the ink for two years or more is less than about 400nm preferably. Such a particle size is obtained by being prolonged and shearing a pigment particle using a small tumbling media. The spherical particle of stainless steel, a zirconium silicate, a zirconium oxide, glass, and plastics is contained in the typical medium used for manufacture of pigment ink. It may wear out, and may mix into ink dispersion liquid, and the particle with the large surface area used at this trituration process may pollute the last prescription. Although this contamination is based also on a kind and an amount, it may have a bad influence on the property of ink. For example, the stability fall of the ink function to lead etc. may produce the change of pH by reacting by contamination with discoloration of color pigment prescription (especially light color, such as yellow), and the chemicals of prescription of a medium, the difficulty of ink filtration, and the useful life longevity of a printing cartridge. A desirable tumbling media is a high-density spherical ceramic particle of a high degree of hardness which has a smooth and uniform front face highly. In order to use it for manufacture of the ink of this invention, especially a desirable tumbling media is a material which Japanese ***** business manufactures and SE Firestone ASOSHIETSU of Philadelphia is marketing under the name of a YTZ ceramic bead. This material is the spherical ceramic particle which carried out yttrium processing of the core of the zirconium oxide of a high grade, and raised abrasion resistance. It has a very smooth and uniform front face, and this particle is a perfect globular form and a degree of hardness is [density is 6.0 g/cm³ and] 91. The example of the process of such a material is indicated by the open JP,57-191234,A specification and the JP,56-145118,A specification of November 11, 1981 public presentation on November 25, 1982 appended to this specification as reference.

[0061] The following example shows manufacture and the usage of the ink constituent of this invention in detail. These detailed explanation is within the limits of the above-mentioned still more general explanation, and illustrates this. These examples are only the purposes of explanation and do not limit the range of this invention.

[0062] The polymer dispersant (it is hereafter described as "Terpolymer L") which has the following general formula was used for the ink constituent of example 1 this invention.

[0063]

[Formula 18]

[0064] (1) The manufacture terpolymer L of Terpolymer L was generated as follows. Poly dimethylsiloxane (PDMS-MA) 7.84g which has a monochrome metacryloxy propyl group in 22.8g (265 millimole) of methacrylic acids, and an end group (8.7 millimole) Molecular weight 900, stearyl methacrylate 2.95g (8.7 millimole), Dodecane thiol 2.06g (9.9 millimole), dimethyl-2,2'-azobisisobutyrate 0.64g (2.84 millimole). And after deaerating an isopropyl alcohol 100ml solution with an argon (the process filled up with an argon in part using the Firestone bulb after exhaust air is repeated), it was heated at 70 degrees C for 16 hours. It added gradually, stirring to a 1.0l. hexane at high speed, after cooling this mixture to a room temperature. Filtration under reduced pressure of the obtained solid-state was carried out, it dissociated, and overnight dryness was carried out at 80 degrees C into the vacuum. Reaction yield was about 85%. Protons NMR and GPC determined the property of this copolymer.

[0065] The undiluted solution of a dispersant was generated as follows. 400ml beaker into which 40g of deionized water was put was laid on the hot plate with a magnetic stirrer. After adding into a beaker, stirring terpolymer L12g, 18g of KOH solutions was added to this 20%. This mixture was heated at 50 degrees C for 2 hours. When there was need, the KOH solution was added 20% and pH was adjusted to 7.5. Next, deionized water was added and the above-mentioned undiluted solution weight was set to 100g (terpolymer L12%).

[0066]

Prescription A Component Amount Carbon black (Cabot Corp., MONAKU 800) 26.0g Terpolymer L undiluted solution 54.0g Deionized water 100.0g prescription B Component Amount Carbon black (Degussa AG and SUPESSHARU black 4A) 26.0g Terpolymer L undiluted solution 54.0g Deionized water 100.0g [0067] Prescription A and B was prescribed as follows. It front-mixed by stirring a component mechanically until a lump disappears beforehand. This mixture was distributed at the rate of 700rpm with the SHIEGUBARI grinding machine model 01std type with a zirconium-silicate shot of 10-12 meshes. Although usually carried out for at least 1 hour, this grinding process has temperature controlled and can also be performed more for a long time. The terpolymer concentrate was taken out from the grinding machine, deionized water was added, and the last solid content was made 12%.

[0068] The dispersion liquid which described Prescription A were used and the ink constituent which has the following component was prepared.

Carbon black 4% (weight)

Terpolymer L 1% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water 75% [0069] The ink constituent was prepared in the following procedure.

(1) Deionized water, PEG and 1, and 3-propanediol was mixed for 20 minutes.

(2) It added into the above-mentioned mixture, stirring a terpolymer concentrate (prescription A). Stirring was continued for 20 minutes.

(3) The 20%KOH solution was added and pH of a constituent was adjusted to 8.3.

(4) It filtered by 1.2 micrometer.

[0070] This ink was used by the ink jet printer, and when it printed and examined on six typical kinds of different papers, a good maintenance property, good optical density, and the desirable advanced printing property were shown.

[0071] The ink constituent which has the following component using Prescription B and the process of a publication in the example 2 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% Polyethylene glycol (molecular weight 400) 14% 1, 3-propanediol 6% Deionized water This ink was used by the ink jet printer 76.25%, and when it printed and examined on six typical kinds of different papers, good optical density, the good maintenance property, and the desirable advanced printing property were shown.

[0072] The ink constituent which has the following component using Prescription A and the process of a publication in the example 3 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water When this ink was used by the conventional ink jet printer 76.25%, the printed matter in which a good maintenance property is shown and a series of desirable advanced printing properties are shown with good optical density was obtained.

[0073] The ink constituent which has the following component using Prescription B and the process of a publication in the example 4 example 1 was prepared.

Carbon black 3% Terpolymer L 1% Brand name Liponic EG-1 10% 1, 3-propanediol 10% Deionized water When this ink was used by the conventional ink jet printer 76%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, the outstanding (good optical density is included) printing property was shown.

[0074] The ink constituent which has the following component using Prescription B and the process of a publication in the example 5 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water When this ink was used by the ink jet printer 76.25%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0075] The ink constituent which has the following component using the process of a publication in the example 6 example 1 was prepared.

Carbon black (FW18, Degussa AG, a Ridgefield park, N.J.) 3% Terpolymer L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water When this ink was used by the conventional ink jet printer 76.25%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0076] The ink constituent which has the following component using the process of a publication in the example 7 example 1 was prepared.

Carbon black (FW18) 3% Terpolymer L 0.75% 1, 3-propanediol 10% Brand name Liponic EG-1 10% Brand name Kathon PFR (A destruction-of-life agent, loam & Haas) 0.15% Deionized water When this ink was used by the conventional ink jet printer 76.10%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0077] The ink constituent which has the following component using the process of a publication in the example 8 example 1 was prepared.

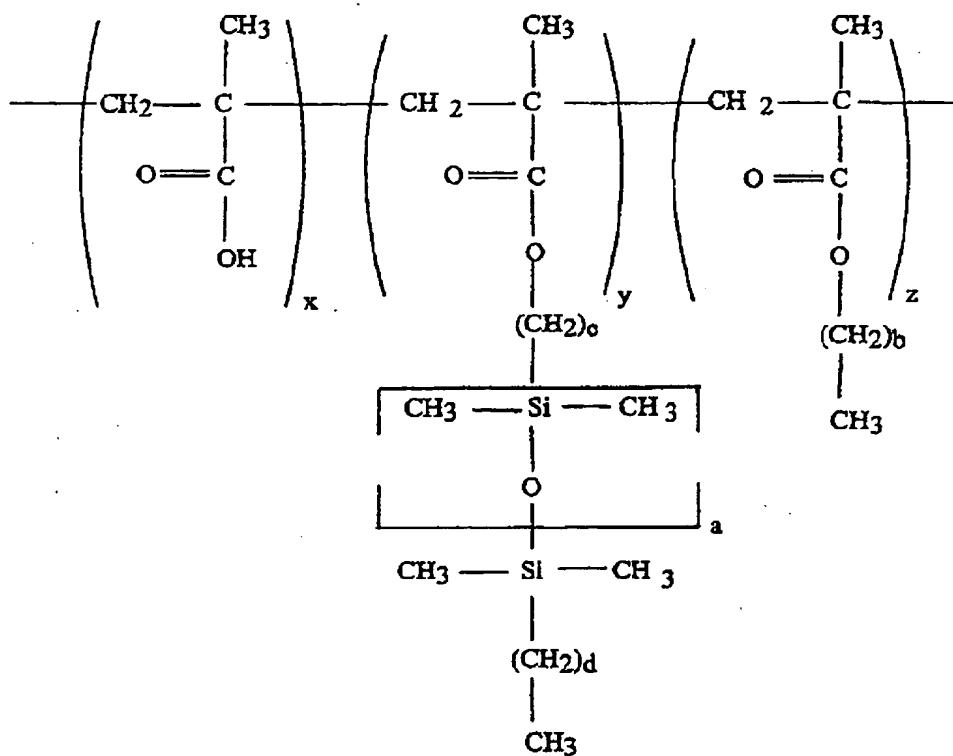
Carbon black (SUPESSHARUBURAKKU4A) 3% Terpolymer L 0.75% 1, 4-butanediol 10% Polyethylene glycol (molecular weight 600) 10% n-propanol 0.2% Deionized water When this ink was used by the conventional ink jet printer 75%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0078] Examples 9-11 were prepared by the same method as the example 3 explained except having used 1,5-pentanediol, 1, and 6-hexanediol and 1, and 7-heptane diol instead of examples 9-111 and 3-propanediol. When it was used by the conventional ink jet printer, the obtained ink constituent showed the good maintenance property, and when it printed and examined on six kinds of typical papers, it showed good optical density.

[0079]

[Effect of the Invention] The ink of examples 1-11 had the average optical density of about 1.35 at least (as measurement in the Macbeth DENSHO meter). This ink showed the good maintenance property and the printing property again. "A good maintenance property" means not being formed at all on the ink-jet print head after the by-product of the remains ink which cannot move printing, and this by-product is investigated by the visual inspection of printing data, and causes inferior printing quality. "A good printing property" is that the ink drop which is not desirable does not exist by the investigation by the visual inspection while meaning the level which can permit feathering. The conventional ink which does not have the auxiliary solvent of this invention does not show the average optical density of about 1.35 simultaneously at least in addition to an above-mentioned good maintenance property and an above-mentioned printing property.

[Formula 19]



[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the ink constituent used for an ink jet printer.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Ink-jet printing is performed by injecting ink from a nozzle to paper or other print media. Ink can be made to inject by various kinds of methods towards a medium. For example, in electrostatic printing, ink is injected by the electrostatic field towards a medium from a nozzle. In the procedure of other ink-jet printings known as a squeeze tube, the piezoelectric device is used into an ink nozzle. Ink is transported to print media through a nozzle by the electric distortion of a piezoelectric device. In the procedure of other ink-jet printings in which thermal ** is known as bubble ink-jet printing, when the bubble of a gaseous phase expands within a nozzle, ink is injected towards print media from a nozzle. The print processes of these various kinds are indicated by issue (refer to Chapter 13 "ink-jet printing" especially) in DABEKU and edited by Shache "hard copy output unit", and Academic Press 1988.

[0003] The ink constituent used for an ink jet printer usually contains the organic solvent of deionized water, water solubility, or water and compatibility, and a coloring agent. Generally, a coloring agent is the color of fusibility. There are many problems [the chemicals-proof nature with low thermal stability whose printing quality is not good is low and] of being easy to oxidize including bleeding, feathering, etc. of ink which plugging produces in an injection channel by the evaporation of a solvent which is not [with low water resistance] good, or change of the solubility of a color and which a color crystallizes in the ink [it is regrettable and] which contains a fusibility color especially.

[0004] Many of these problems are solvable by using an insoluble pigment instead of the fusibility color used for ink prescription. Generally, the pigment is excellent in the property as compared with the color, and excellent in respect of the ability to also suit especially water resistance, lightfastness, thermal stability, oxidation stability, and the paper coated or processed also at a regular paper. However, in order not to dissolve in an ink constituent, therefore to make it distribute, some new problems produce a pigment. The stability of ink is very important for maintaining the homogeneity of a property, and a row in the point of making it both not get a pigment blocked in an ink jet, while not using it. It is ideal to make the amount of a pigment required in an ink constituent, of course into the minimum from the reason of both stability and cost. However, if the amount of the pigment in an ink constituent is reduced, the optical density of a picture will fall. Furthermore, in order to secure required stability, while the balance of composition is required, therefore has suitable viscosity in an ink jet printer using a constituent, when it prints on paper, it is important [water resistance and lightfastness are good, and] that running and feathering are also the minimum. It was very difficult to develop ink prescription which optimized all of these properties until now. Adjusting the dispersant and solvent system of an ink constituent for the purpose of maintaining and optimizing the balance of these properties that conflict in many cases as common practice was performed. However, prescription which optimized all these properties, without using a specific polymer dispersant before this invention was not attained.

[0005] The ink constituent for ink jets which contains the auxiliary solvent of an aquosity carrier medium, pigment dispersion liquid, and a polyol and an oxidization alkylene in the U.S. Pat. No. 5,180,425 specification of the matric on January 19, 1993 is indicated. The life of ink jet printer ability is lengthened and these ink is taught that there is a coat-proof plasticity. RAIPo nick EG-1 is one of the indicated desirable auxiliary solvents. The polyethylene glycol is contained in other solvents used for this patent.

[0006] Pigment dispersion liquid, the aquosity carrier medium, and a polyol, the condensation product of an oxidization alkylene and the ink constituent containing the auxiliary solvent mixture containing a cyclic-amide derivative for ink jets are indicated by the U.S. Pat. No. 5,302,197 specification of wick Lamasim NAIKE on April 12, 1994. It is taught that RAIPo nick EG-1 is useful as a condensation-product component of a polyol and an oxidization alkylene.

[0007] An aquosity carrier medium, a specific alkyl polyol ether auxiliary solvent, and the ink for ink jets that consists of pigment dispersion liquid (what stabilized the pigment particle with the dispersant) are indicated by the Europe patent No. 603,469 application of Chillan and others on June 29, 1994. It is taught that these ink has viscosity, surface tension, plugging prevention of a nozzle, printing quality, light stability, bleeding-proof nature, and waterproof good balance. 1, 2, and 3-butane triol is contained in the solvent used by invention of an indication.

[0008] A clear image is formed in the U.S. Pat. No. 4,597,794 specification of OTA and others on July 1, 1986, and ink prescription used for the ink-jet printing process said to have a good physical property is indicated. A polyethylene glycol and 1, 2, and 6-hexane triol are contained in the solvent indicated especially in order to use it for this ink.

[0009] Giving characteristic mixture, when optimizing a property was found out by using the specific auxiliary solvent mixture which contains C2-C8 end alkane diols or such mixture with either the polyethylene glycol of (a) low

molecular weight, a related compound or the condensation product of the (b) polyol and an oxidization alkylene for the water-color-ink constituent containing the dispersion liquid of an insoluble pigment. Especially, the property these constituents excelled [property] in stability, optical density, viscosity, the printing property (running of feathering in water resistance and the printed page and ink is the minimum), and the row in points, such as a problem (the blinding of the printer jet at the time of printer un-using it is the minimum) of printer maintenance, (even when low pigment concentration is used) is acquired. About the combination of the specific auxiliary solvent shown by this invention, neither a publication nor suggestion has each in the above-mentioned patent.

[Translation done.]

* NOTICES *

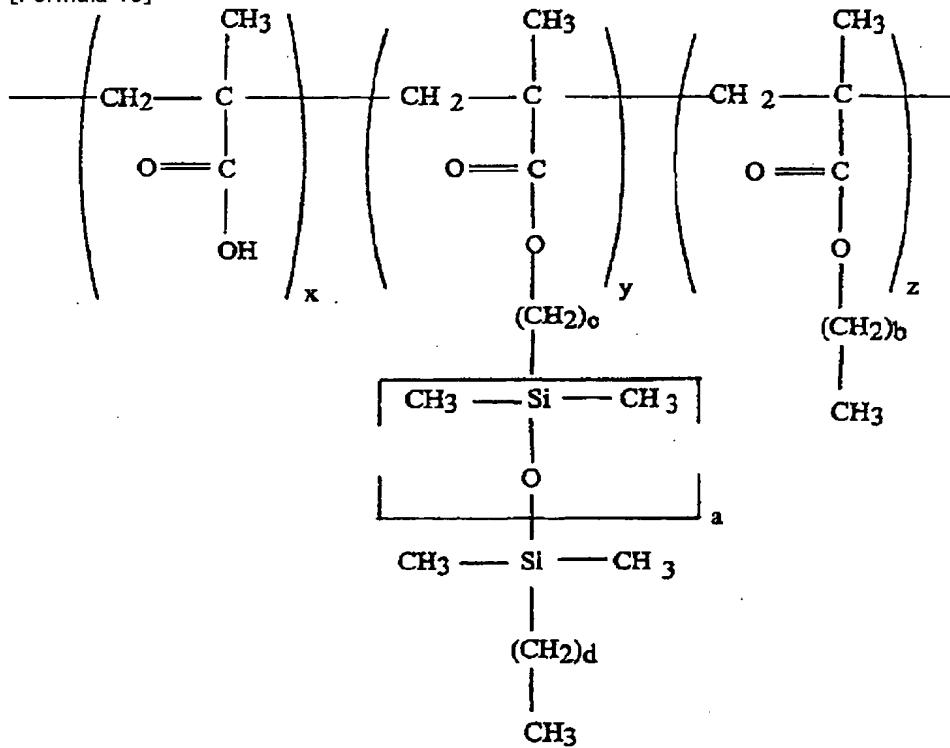
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EFFECT OF THE INVENTION

[Effect of the Invention] The ink of examples 1-11 had the average optical density of about 1.35 at least (as measurement in the Macbeth DENSHO meter). This ink showed the good maintenance property and the printing property again. "A good maintenance property" means not being formed at all on the ink-jet print head after the by-product of the remains ink which cannot move printing, and this by-product is investigated by the visual inspection of printing data, and causes inferior printing quality. "A good printing property" is that the ink drop which is not desirable does not exist by the investigation by the visual inspection while meaning the level which can permit feathering. The conventional ink which does not have the auxiliary solvent of this invention does not show the average optical density of about 1.35 simultaneously at least in addition to an above-mentioned good maintenance property and an above-mentioned printing property.

[Formula 19]



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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is to offer the pigment ink constituent with which it has been improved for [containing a specific auxiliary solvent system] ink jet printers.

[Translation done.]

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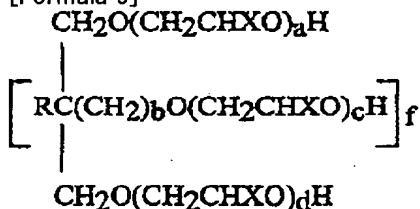
MEANS

[Means for Solving the Problem] Other purposes and features of this invention become clear by the following indication.

[0012] this invention is the insoluble pigment of 0.01% – about 20.0% of (a) abbreviation:
(b) About 0.001% – about 40.0% of polymer dispersant for the aforementioned pigments;
(c) It is related with the water–color–ink constituent containing about 1.0% – about 75.0% of auxiliary solvent mixture containing about 40.0% – about 99.0% of water carrier; and (d) (1) C2–C8 end alkane diols or such mixture, and the matter chosen from the group which consists of (2) following (i) – (iii) suitable for use of an ink jet printer.
(i) Condensation product of a polyol / oxidization alkylene which has about 200 – about 5,000 molecular weight and which has the mixture of a polyethylene glycol and a polypropylene glycol, and the formula of (ii) following in a polyethylene glycol and a row.

[0013]

[Formula 9]



[0014] here — X — H or C1 – C6 alkyl, and R — H, C1 – C6 alkyl, or $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})$ — eH, b0 or 1, and a+d+f (c+e) — about 2 – about 100 f — about 1 – it is about 6
(iii) Such mixture.

In addition, above-mentioned (1) ratio [of : (2) / weight] (1): (2) is about 95:5 – abbreviation 5:95.

[0015] The percentage and the ratios which were used for this specification are “weight %” and a “weight ratio”, unless it otherwise specifies. The molecular weight used for this specification is number average molecular weight, unless it otherwise specifies. A C2–C8 end alkane diol is defined as each end as what means the diol which has a hydroxy group, for example, the alkane diol which has the following formula.

[0016]

[Formula 10]



Here, t is about 0 – abbreviation 6.

[0017]

[Embodiments of the Invention] this invention relates to the water–color–ink constituent suitable for using it for an ink jet printer. These constituents contain the polymer dispersant (a pigment and a dispersant exist in the constituent as dispersion liquid), the aquosity carrier, and the specific auxiliary solvent mixture for a coloring agent (for example, carbon black, cyanogen, a Magenta, or a yellow pigment) like an insoluble pigment, and a pigment. Each of these required components is explained in detail below with some additional components.

[0018] a polymer dispersant — the constituent of this invention — setting — about 0.001% – about 40.0% of the last component — it is contained about 0.5% to about 5.0% most preferably about 0.25% to about 10.0% both the anion nature by which it is known for the industry that it is suitable for using it for the polymer dispersant suitable for using it by this invention as a dispersant of the ink manufacture object for ink jets cation nature and a non-ionicity polymer — although — it is contained The example of such a material is indicated by the U.S. Pat. No. 5,310,778 specification of Shore and others on May 10, 1994 appended to this specification as reference. A homopolymer, a copolymer, the letter polymer of branching, or a graft polymer is sufficient as such a polymer dispersant. Moreover, a random polymer or a block polymer is sufficient.

[0019] The block copolymer of AB, BAB, and ABC is one sort of a polymer dispersant useful to this invention.

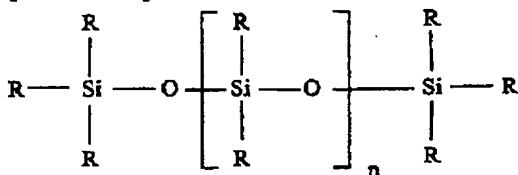
Desirable things are AB and BAB which were guided from at least one sort of alkyl acrylics or a methacrylic ester and an amine substitution acrylic, or the monomers of a methacrylic ester, and an ABC block copolymer. Desirable AB and BAB block copolymers, and these processes are indicated by the U.S. Pat. No. 5,085,698 specification of MA and others on February 4, 1992 appended to this specification as reference.

[0020] A polymer dispersant useful to operation of this invention usually tends to combine a hydrophobic segment with the pigment particle in an ink constituent including both polymer segments of a hydrophobic property and a hydrophilic property, it is tended by the liquid ink medium to carry out the solvation of the hydrophilic segment, and it stabilizes dispersion liquid according to these, a three-dimensional mechanism, and/or an ionicity mechanism.

[0021] The desirable polymer dispersant of a kind used by this invention contains the block or graft copolymer containing a hydrophilic polymer segment and the hydrophobic polymer segment which contains a stable siloxyl substituent to hydrolysis. Especially a desirable thing is a graft copolymer containing a hydrophilic polymer segment (especially acrylate or a methacrylate copolymer) and the hydrophobic polymer segment guided from the macromere which has the following formula among the groups of these dispersants.

[0022]

[Formula 11]



[0023] n is the low-grade alkyl (C1-C6) or siloxyl which 2-16R became independent of, respectively among a formula. Such material is indicated by the U.S. patent application 08th/No. 360,199 specification of December 21, 1994 and beaches appended to this specification as reference.

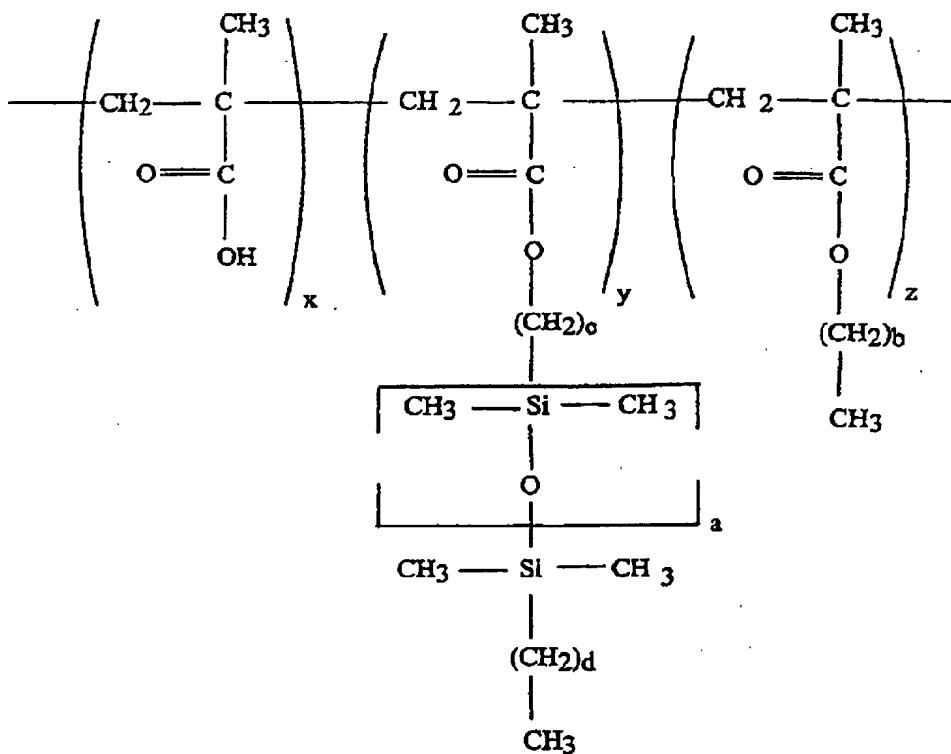
[0024] The desirable polymerization nature powder of other kinds is a graft copolymer containing the hydrophobic polymer segment which has about 600 – about 20,000 molecular weight, has a stable siloxyl substituent to (a) hydrophilic-property polymer segment and (b) hydrolysis, and has about 400 – about 3,000 molecular weight, and the stabilization segment chosen from the group which becomes a row from the surface activity macromere of (c) reactivity, protective colloid macromere, and a non-siloxyl hydrophobic monomer.

[0025] Desirable monomer ratio (a) : (b) is about 10:1 – abbreviation 100:1, and ratio [of a desirable monomer] (b): (c) is about 2:1 – abbreviation 1:5. A desirable hydrophilic polymer segment has a bitter taste relay torr or the most desirable meta-chestnut rhe torr polymer matter including a carboxy substituent. A desirable siloxane content hydrophobic polymer segment is macromere of the poly dialkyl siloxane which has an acryloyl or a methacryloyl machine at the end. The most desirable hydrophobic segment is ** which has about 400 – about 2,000 molecular weight, and has a dimethyl polysiloxyl machine. A desirable stabilization segment Stearylacrylate, stearyl methacrylate, Laurylacrylate, lauryl methacrylate, nonyl-phenol acrylate, Nonyl-phenol methacrylate, n — about 1- nonyl phenoxy poly (ethyleneoxy) n methacrylate which is about 40; n — about 1- nonyl phenoxy poly (ethyleneoxy) n acrylate which is about 40; n — about 5- methoxy poly (ethyleneoxy) n methacrylate which is about 40; Methoxy poly whose n is about 5 – abbreviation 40 (Ethyleneoxy) n acrylate; Stearyl oxy-poly whose n is about 1 – abbreviation 20 (Ethyleneoxy) n methacrylate; Stearyl oxy-poly whose n is about 1 – abbreviation 20 (Ethyleneoxy) n acrylate; — fluorine-ized C1-C18 alkyl methacrylate; — fluorine-ized C1-C18 alkyl acrylate; — poly (propylene glycol) methyl-ether methacrylate; — poly (propylene glycol) methyl-ether acrylate — Poly (Propylene glycol) 4-nonylphenyl ether methacrylate; — poly (propylene glycol) 4-nonylphenyl ether acrylate; — polyethylene-oxide; which has a metacryloxy machine and a trimethylsiloxy machine at the end — Polyethylene-oxide; which has an acrylic oxy-basis and a trimethylsiloxy machine, and such mixture are included in an end.

[0026] The most desirable thing has the following formula in a principal chain with this kind of polymer dispersant.

[0027]

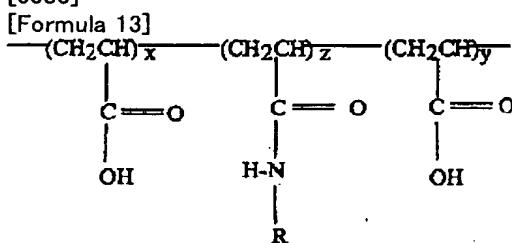
[32] [Formula 12]



[0028] The inside of a formula, 3; x — about 5— about 100 — desirable — about 15 — about 50 y — about 1— about 2 — desirable — about 1 z — about 1— about 5 — desirable — about 1 —; a — about 3— about 45 — desirable — about 9 b — about 3— about 29 — desirable — about 15 — about 17 c — about 2— about 8 — desirable — about — d — 0— about 7 — it is about 3 preferably These polymer dispersants are indicated by the U.S. patent application "the polymer dispersant for pigment use ink" of ***** of the beaches appended to this specification as reference. The end group of the dispersant of this invention is not limited. For the purpose of explanation, it is contained like [a thio substitution hydrocarbon] hydrogen.

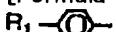
[0029] The polymer dispersant of other kinds is indicated by the U.S. patent application 08th/No. 360,200 specification of December 21, 1994 and beaches appended to this specification as reference. These matter is the graft polymers containing the hydrophobic segment side chain which has one side chain combined with one principal chain as preferably as the principal chain of the hydrophilic polyacrylic acid of the weight average molecular weight of about 1,000 — about 5,000 between. This kind of desirable polymer has one of the following structure expressions.

[0030]



[0031] the inside of a formula, and $x+y$ — about 20 — about 200 z — about 1 — about 10 R — the alkyl of C6—C36 — — or [0032]

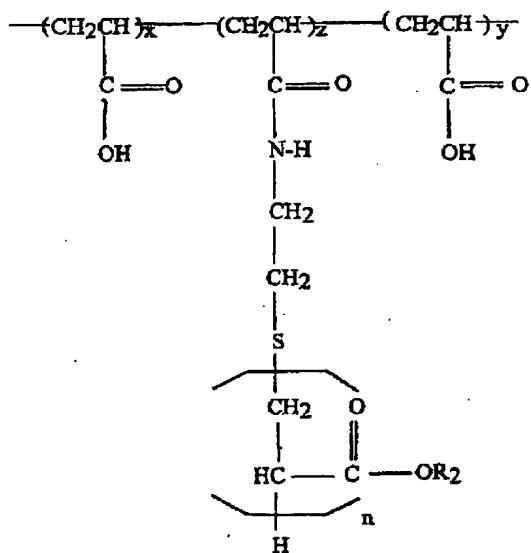
[Formula 14]



R 1 is the alkyl or the following basis of C4—C20 here.

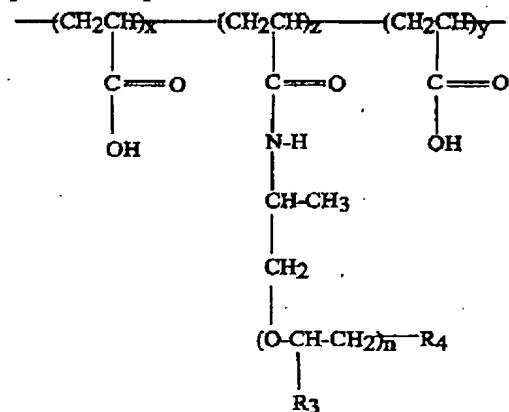
[0033]

[Formula 15]



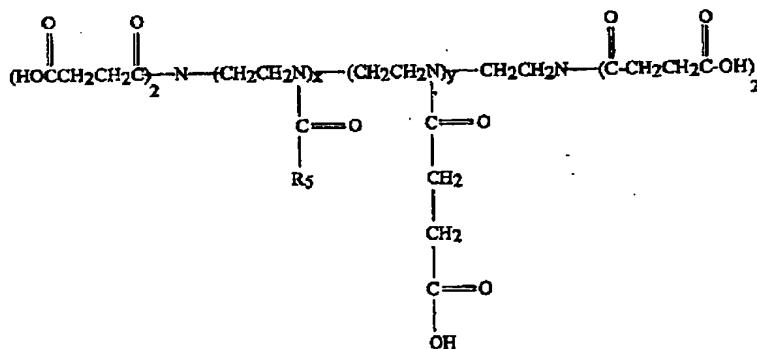
[0034] the inside of a formula, and $x+y$ — about 20 — about 200 z — about 1 — about 10 (it distributed at random) n — about 2 — about 40 and R_2 — an alkyl or an aryl — desirable — butyl — or [0035]

[Formula 16]



[0036] the inside of a formula, and $x+y$ — about 20 — about 200 z — about 1 — about 10 and R_3 — H, or CH₃ and R_4 — H, CH₃, or OCH₃ and n — about 10 — about 60 — or [0037]

[Formula 17]



[0038] y of about 6 — Abbreviation 20 and x is [about 1 — abbreviation 5, and R_5] the alkyls of C₆—C₃₀ among a formula.

[0039] The graft copolymer dispersant of this invention is low molecular weight comparatively, in order to acquire the stability of a particle, and its viscosity needs to be low in order to use it for the stable ink for ink-jet printing. For this reason, the polar-solvent polymerization method for generating a copolymer is chosen. The molecular weight of a copolymer and homogeneity are controlled by such method by maintaining the solubility of not only the copolymer obtained but all start raw materials (it is a chain transfer agent to a free radical initiator, a hydrophobic

property and a hydrophilic monomer, and a row). In order to write a prescription to ink-jet printing and to make a water medium suspend the compounded copolymer, it needs to collect copolymers from the polar organic solvent in reaction mixture, and it is necessary to make it dissolve them in water. The copolymer recovery method from a typical polar polymerization solvent includes the following processes.

1. The solution of a copolymer is added to non-solvents, such as a hexane, a polymer is settled from a solution, this refines a copolymer, vacuum filtration of the 2. precipitate is carried out, and 3. copolymer precipitate is dried.

[0040] Next, copolymer powder can be dissolved in a water base and it can be used for generation of the ink for ink-jet printing. This method has high cost and is superfluously complicated. [of cost]

[0041] The desirable method for collecting the dispersants of a copolymer from a polar organic polymerization solvent improves printing quality which decreases it not only merely collects the dispersants of a copolymer, but that the ink-jet ink generated from these dispersants forms a satellite and a splatter. Specifically, these desirable methods include the following process.

1. Dissolve in a water base and exchange 2. solvent, after evaporating a solvent.

[0042] At solvent evaporation and a dissolution process, vacuum tray dryness, rotation evaporation dryness, drum dryness, a turning-circle cylinder vacuum drying, or spray drying evaporates a polar solvent from a copolymer first by the standard method of changing the solution of a copolymer into dryness powder. Next, the dry copolymer powder is dissolved in a water base, and it enables it to use it for generation of the ink of the pigment for ink jets.

[0043] a solvent exchange-buffering-method process — about 35% — about 60% of the polar solvent in a polymerization reactor (preferably about 50%) — distillation — removing — deionized water and a water base (for example, KOH solution) — adding — pH — about 4.5- about 6.5 — it adjusts to about 5 preferably In the case of a polar solvent with the boiling point lower than water, in order to make a solvent distill, the temperature of this mixture is slowly raised, until temperature amounts to about 100 degrees C from which all polar solvents are removed. (This process cannot be used when the boiling point of a polar solvent is higher than the boiling point of water.) further — a water base (for example, KOH solution) — this solution — in addition, pH — about 7- about 8.5 — about 7.5 is raised preferably Subsequently, this solution is used for prescription of the pigment ink for ink jets.

[0044] The 2nd component of the ink constituent of this invention is a pigment which is an insoluble coloring agent. the constituent of this invention — a pigment — the last constituent — receiving — about 0.1% — about 20.0% — about 0.5% — 5.0% exists most preferably about 0.25% to about 10.0% Actually, one of the important advantages of this invention enables prescription of ink which has low pigment concentration (for example, for 0.5% — 5.0%), and moreover, it is quality and is offering the outstanding optical density. All of the well-known conventional pigment can be used in this industry that is indicated as a pigment useful to operation of this invention by the U.S. Pat. No. 5,085,698 specification of February 4, 1992, MA and others appended to this specification as reference. Even if it uses it independently, you may use a pigment, combining.

[0045] The particle of a pigment needs to have [an ink-jet printer, especially a diameter] small ink enough so that the inside of the injection nozzle which is usually about 10 micrometers — about 100 micrometers can be flowed freely. Particle size affects the distributed stability of an important pigment through the life of ink again. The Brownian motion of a particle is useful to condensation prevention of a particle, and, thereby, a product is stabilized further. In order to make color intensity and gloss into the maximum, it is also desirable to use a small particle. A useful size range is about 0.05 microns — about 15 microns. The range of the particle size of a pigment is about 0.05 microns — about 5 microns, and the range of it is about 0.05 microns — about 1 micron most preferably. A pigment can be used also with the form which carried out [the dry form or] humidity. For example, a pigment is usually manufactured in a water medium and is obtained as a filter press cake containing water. With the form of this filter press cake, a pigment is not condensed like [in the case of a dryness form]. Therefore, the pigment of the form of the filter press cake containing water does not need to perform solution condensation in the manufacturing process of ink like [at the time of using the dry pigment].

[0046] The particle of a metal or a metallic oxide can also be used for operation of this invention. For example, the metal and the metallic oxide are suitable for manufacture of the ink for magnetic ink jets. The oxide of a particle, for example, a silica, an alumina, a titania, etc. can be used. Furthermore, the pulverized metal particles, for example, copper, iron, steel, aluminum, and alloys can be chosen because of a suitable use.

[0047] there are inorganic pigments, such as organic pigment; titanium oxide, such as color lake; nitroglycerine pigments, such as polycyclic formula pigment; basic dye lakes, such as azo pigment; phthalocyanine pigments, such as an azo lake, insoluble azo pigment, a disazo condensation pigment, and a chelate azo pigment, a perylene pigment, an anthraquinone pigment, a Quinacridone pigment, a diaxazine pigment, a thio indigo pigment, an isoindolinone pigment, and a KINOFUTARON pigment, and an acid-dye lake, an oximido pigment, an aniline black, and a daylight fluorescent pigment, an iron oxide, and carbon black, etc. in the A desirable pigment contains titanium oxide, an iron oxide, and carbon black in using it in this invention. For the example of the available pigment of marketing which can be used in this invention Brand name Heliogen Blue L 6901F (BASF), Brand name Heliogen Blue NBD 7010 (BASF), Brand name Heliogen Blue K7090 (BASF), brand name Heucophthal Blue GXBT-583D (HYU back), Brand name Irgalite Rubin 4BL (Ciba-Geigy), Brand name Quindo A Magenta (Mobey), a brand-name Indofast brilliant scarlet (Mobey), Brand name Hostaperm Scarlett GO (Hoechst), Permanent Rubin F6B (Hoechst), brand name Monastral Scarlett (Ciba-Geigy), A brand name Raven1170 (COL KEMU), SUPESSHARU black 4A (Degussa AG), Black FW18 (Degussa AG), brand name Sterling NS Black (Cabot), Brand name Sterling NSX 76 (Cabot) Monarch880 (Cabot), Brand name Tipure R-101 (E. I. du Pont de Nemours), MOGARUL (Cabot) BK 8200 (pole URITCHI) Brand name Heliogen Green K 8683 (BASF), Brand name Heliogen Green L9140 (BASF), Brand name Monastral Red B (Ciba-

Geigy), brand name Monastral Violet R (Ciba-Geigy) Brand name Hostaperm Orange GR (Hoechst), brand name Paliogen Orange (BASF), L75-2377 Yellow (Sun KEMU) and L74-1357 Yellow (Sun KEMU), Brand-name Hostaperm yellow H4G (Hoechst), brand name Argazin Yellow 5GT (Ciba-Geigy), Permanent Yellow G3 R-01 (Hoechst), brand name Novoperm Yellow FGL (Hoechst), Brand name Chromophthal Yellow 3G (Ciba-Geigy), HANZA Yellow X (Hoechst), brand name Dalamar Yellow YT-858-D (HYU back), HANZA — brilliant Yellow SANFASUTO 15:4 (Sun Chemical) etc. is in 5GX-02 (Hoechst), SANFASUTO 15:3 (Sun Chemical), and a row.

[0048] The 3rd component of the ink constituent of this invention is an aquosity carrier medium. This component is the mixture of water (preferably deionized water) or water, and at least one kind of water-soluble organic solvent. an aquosity carrier component — constituent [of this invention / about 40.0% of] — about 98.99 — about 50.0% — about 80.0% exists preferably Selection of suitable mixture is dependent on the kind of paper in which ink is printed by the drying time required for the requirements for the specific ink prescribed, for example, desirable surface tension, viscosity, the pigment to be used, and pigment ink, and the row etc. As an example of representation of the water-soluble organic solvent which can be chosen (1) Methyl alcohol, ethyl alcohol, n-propyl alcohol, Isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, isobutyl alcohol, furfuryl alcohol, Alcohols; (2) acetones, such as a tetrahydrofurfuryl alcohol, Ketones or keto-alcohols; (3) tetrahydrofurans, such as a methyl ethyl ketone and diacetone alcohol, Ether; (4) ethyl acetate, such as a dioxane, an ethyl lactate, an ethylene carbonate, Ester; (5) diethylene glycols, such as a propylene carbonate, a glycerol, The 2-methyl -2, 4-pentanediol, 1 and 2, 6-hexane triol, Polyhydric alcohol, such as a thiodiglycol; (6) ethylene-glycol monomethyl (or monoethyl) ether, The diethylene-glycol monomethyl (or monoethyl) ether, the propylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl monochrome guided from alkylene glycol, such as the triethylene-glycol monomethyl (or monoethyl) ether and the diethylene-glycol dimethyl (or diethyl) ether, or a diethers; (7) pyrrolidone, a N-methyl-2-pyrrolidone, There are sulfur content compounds, such as nitrogen content cyclic compounds, such as 1-(2-hydroxyethyl)-2-pyrrolidone, 1, and 3-dimethyl-2-imidazolidinone, (8) dimethyl sulfoxide, and a tetramethylen sulfone. There are lactone and lactams in other useful solvents.

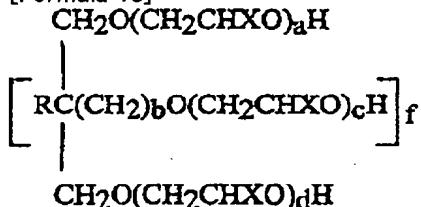
[0049] When using the mixture of water and an organic solvent as a carrier medium by this invention, a medium usually contains about 0.1% of water / water of 99.9% of organic solvent — 99.9% of abbreviation / 0.1% of organic solvent. Desirable ratios are about 50% of water / water of 50% of organic solvent — 90.0% of abbreviation / about 10.0% of organic solvent. Such percentage receives the total weight of a water carrier medium. What is used for a water carrier medium in the term of the "organic solvent" used on these specifications should understand that it is not what means that a specific material used as a component of the auxiliary solvent of this invention is included.

[0050] In the desirable organic solvent used for the water carrier medium component of this invention Ethylene glycol, 1 and 2, 6-hexane triol, a thiodiglycol, Polyhydric alcohol, such as a hexylene glycol and a diethylene glycol; The pentanediol of a non-end (as [give / here / a definition]), Glycol ethers, such as diols; lauric-acid propylene glycols, such as hexandiol and homologous-series diols; Glycerol; and the ethylene glycol monomethyl (or monoethyl) ether, The diethylene-glycol methyl (or ethyl) ether, the triethylene-glycol monomethyl (or monoethyl) ether, The low-grade alkyl ether of which polyhydric alcohol; A methanol, ethanol, Ketones [, such as an alcohols; acetone,], such as propanol and a butanol; A tetrahydrofuran, Ether, such as a dioxane; there are lactams, such as lactone;2-pyrrolidones, such as ester; gamma-butyrolactones, such as ethyl acetate, sulfolanes, and N-methyl pyrrolidone, and a 1-methyl-2-pyrrolidone. Although an organic solvent gives useful properties, such as shortening of the drying time, reduction of bleeding, and increase of permeability, to an ink constituent, generally (the auxiliary solvent matter defined as this specification is a difference), optical density, the stability of a constituent, or printing quality is not improved. A glycerol, a thiodiglycol, n-propanol, and such mixture are in a desirable organic solvent especially.

[0051] The component of the last required to use it with the constituent of this invention is auxiliary solvent mixture, and occupies about 10.0% — about 30.0% most preferably about 5.0% to about 30.0% 1.0% — about 75.0% of abbreviation of the last constituent. This auxiliary solvent mixture contains the C2-C8 end alkane diols which are the first component, or such mixture. Furthermore, the polyethylene-glycol type compound which is the second component, the condensation product of a polyol and an oxidization alkylene, or the mixture of these compounds is also contained. the 2nd component used for this auxiliary solvent mixture — molecular weight — about 200- about 5,000 — it is the mixture of about 200 — about 3,000 polyethylene glycol or a polyethylene glycol, and a polypropylene glycol preferably It is the polyethylene glycol which a polyethylene glycol (PEG) is used most preferably and has about 200 to 1,000 molecular weight preferably. The 2nd component of an auxiliary solvent may be a condensation product of a polyol and an oxidization alkylene which has the following formula.

[0052]

[Formula 18]



[0053] the inside of a formula, and x — H, or CH₃ and R — the alkyl of H, C₁-C₄, or -CH₂O (CH₂CH₂O) — eH, b₀ or 1, and a+d+f (c+e) — about 2 — about 100 f — about 1— it is about 6

[0054] The condensation product of a useful polyol and a useful oxidization alkylene is a resultant of a polyol and an oxidization alkylene in this invention. These are indicated by the U.S. Pat. No. 5,180,425 specification of January 19, 1993 and matic appended to this specification as reference. Solubility [usually as opposed to water in these compounds] is about 4.5% (4.5 sections [as opposed to / the water 100 section / Namely,]) at least at 25 degrees C. The oxidization alkylene used for these compounds is the mixture of an ethyleneoxide, a propylene oxide, or both oxides. Although the mixture of the compound with which the degrees of oxy-alkylation differ is produced by the reaction with a single oxidization alkylene, the shown structure is based on the average composition containing a series of oxidization alkylene units. The random and block copolymer of a propylene oxide and an ethyleneoxide can be used. The oxidization alkylene and the polyol which reacted may have three or more hydroxyl groups. Useful triol is a glycerol, a trimethylol propane, and trimethylethane. Other triol, such as 1, 2, and 4-butane triol and 1, 2, and 6-hexane triol, can be used. Useful tetrols have a pentaerythritol, 1,1-trimethylol propane, a methyl glucoside, etc. A glucose, a pen toll, etc. can be used. A sorbitol is useful HEKISORU. Other useful HEKISORU has a JIPENTA erythritol and an inositol. Usually, since such a condensation product is not compatibility, generally it is not suitable for the oxidization alkylene condensation product of a diol to pigment dispersion liquid for using it by this invention. One of the exception of the is a condensation product with the oxidization alkylene of neopentyl glycol.

[0055] There are the following in the example of the condensation product of a polyol and an oxidization alkylene.

[0056]

[Table 1]

表

製品	R	a + d + f		
		(c + e)	b	f
Liponic®EG-1 ¹	-H	26	0	1
Liponic®SO-20 ¹	-H	20	0	4
Photonol®PHO-7149 ²	-C ₂ H ₅	2.7	1	1
Photonol®PHO-7155 ²	-C ₂ H ₅	7.4	1	1
Voranol®230-660 ³	-CH ₃	3.0	1	1
Voranol®234-630 ³	-C ₂ H ₅	3.0	1	1
Fomrez®T-279 ⁴	-C ₂ H ₅	3.1	1	1
Fomrez®T-315 ⁴	-C ₂ H ₅	4.1	1	1

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N. Y.

[0057] The condensation product of a polyol and an oxidization alkylene especially desirable although it is used by this invention is above Liponic. It is EG-1. This material has the name of CTFA of GURISERESU-26, is what added the 26-mol ethyleneoxide to the glycerol, and is marketed from a RIPO Chemicals company, Paterson, and New Jersey.

[0058] The first of auxiliary solvent mixture and the second component exist by the weight ratio (the first component : the second component) of about 90:10 - abbreviation 10:90. the weight ratio of a PEG:diol optimal when auxiliary solvent mixture contains a polyethylene-glycol (PEG) type compound and a C₂-C₈ end alkane diol — about 50:50- it is about 70:30 The condensation product optimal when auxiliary solvent mixture contains the condensation product of a polyol and an oxidization alkylene with C₂-C₈ end alkane diols or such mixture: Diol ratios are about 95:5 - abbreviation 5:95. The ratio of the general most desirable assistant solvent mixture is about 40:60-60:40.

[0059] In order to manufacture such a constituent, you may prepare the ink constituent of this invention by what method learned for this industry. The important point of this constituent is that a pigment and a polymer dispersant form stable dispersion liquid in an aquosity carrier and an auxiliary solvent mixture. By one method both, a polymer dispersant is first mixed with a pigment, next it grinds with a grinding machine, and a particle is decreased to permission particle size. Next, this material is mixed with other ink components. The ink of predetermined concentration is obtained. A surfactant can be added by request, distribution of a pigment can be raised, the surface tension of ink can be changed, and osmosis on paper can be controlled. There are non-ionicity, amphotericism, and an ionic surfactant in a suitable surfactant. In order to acquire the advantage from which other additives, for example, a destruction-of-life agent, the wetting agent, the chelating agent, the viscosity controlling agent, etc. were known for

this industry, it can add to this ink constituent by the operating concentration established in this industry. Generally, in order to promote distribution of a pigment, it is desirable to manufacture Ink-jet, Inc. in the concentration gestalt containing the pigment. Subsequently, it dilutes to suitable concentration to use this ink by the ink jet and the printing system.

[0060] By the method of generating the pigment ink for ink jets, it is required to usually decrease the size of a particle using a trituration mill. The particle size of a pigment needs that less than about 200nm of demands of the self-stable life of the ink for two years or more is less than about 400nm preferably. Such a particle size is obtained by being prolonged and shearing a pigment particle using a small tumbling media. The spherical particle of stainless steel, a zirconium silicate, a zirconium oxide, glass, and plastics is contained in the typical medium used for manufacture of pigment ink. It may wear out, and may mix into ink dispersion liquid, and the particle with the large surface area used at this trituration process may pollute the last prescription. Although this contamination is based also on a kind and an amount, it may have a bad influence on the property of ink. For example, the stability fall of the ink function to lead etc. may produce the change of pH by reacting by contamination with discoloration of color pigment prescription (especially light color, such as yellow), and the chemicals of prescription of a medium, the difficulty of ink filtration, and the useful life longevity of a printing cartridge. A desirable tumbling media is a high-density spherical ceramic particle of a high degree of hardness which has a smooth and uniform front face highly. In order to use it for manufacture of the ink of this invention, especially a desirable tumbling media is a material which Japanese ***** business manufactures and SE Firestone ASOSHIETSU of Philadelphia is marketing under the name of a YTZ ceramic bead. This material is the spherical ceramic particle which carried out yttrium processing of the core of the zirconium oxide of a high grade, and raised abrasion resistance. It has a very smooth and uniform front face, and this particle is a perfect globular form and a degree of hardness is [density is 6.0 g/cm³ and] 91. The example of the process of such a material is indicated by the open JP,57-191234,A specification and the JP,56-145118,A specification of November 11, 1981 public presentation on November 25, 1982 appended to this specification as reference.

[0061] The following example shows manufacture and the usage of the ink constituent of this invention in detail. These detailed explanation is within the limits of the above-mentioned still more general explanation, and illustrates this. These examples are only the purposes of explanation and do not limit the range of this invention.

[0062] The polymer dispersant (it is hereafter described as "Terpolymer L") which has the following general formula was used for the ink constituent of example 1 this invention.

[0063]

[Formula 18]

[0064] (1) The manufacture terpolymer L of Terpolymer L was generated as follows. Poly dimethylsiloxane (PDMS-MA) 7.84g which has a monochrome metacryloxy propyl group in 22.8g (265 millimole) of methacrylic acids, and an end group (8.7 millimole) Molecular weight 900, stearyl methacrylate 2.95g (8.7 millimole), Dodecane thiol 2.06g (9.9 millimole), dimethyl-2,2'-azobisisobutyrate 0.64g (2.84 millimole), And after deaerating an isopropyl alcohol 100ml solution with an argon (the process filled up with an argon in part using the Firestone bulb after exhaust air is repeated), it was heated at 70 degrees C for 16 hours. It added gradually, stirring to a 1.0l. hexane at high speed, after cooling this mixture to a room temperature. Filtration under reduced pressure of the obtained solid-state was carried out, it dissociated, and overnight dryness was carried out at 80 degrees C into the vacuum. Reaction yield was about 85%. Protons NMR and GPC determined the property of this copolymer.

[0065] The undiluted solution of a dispersant was generated as follows. 400ml beaker into which 40g of deionized water was put was laid on the hot plate with a magnetic stirrer. After adding into a beaker, stirring terpolymer L12g, 18g of KOH solutions was added to this 20%. This mixture was heated at 50 degrees C for 2 hours. When there was need, the KOH solution was added 20% and pH was adjusted to 7.5. Next, deionized water was added and the above-mentioned undiluted solution weight was set to 100g (terpolymer L12%).

[0066]

Prescription A Component Amount Carbon black (Cabot Corp., MONAKU 800) 26.0g Terpolymer L undiluted solution 54.0g Deionized water 100.0g prescription B Component Amount Carbon black (Degussa AG and SUPESSHARU black 4A) 26.0g Terpolymer L undiluted solution 54.0g Deionized water 100.0g [0067] Prescription A and B was prescribed as follows. It front-mixed by stirring a component mechanically until a lump disappears beforehand. This mixture was distributed at the rate of 700rpm with the SHIEGUBARI grinding machine model 01std type with a zirconium-silicate shot of 10-12 meshes. Although usually carried out for at least 1 hour, this grinding process has temperature controlled and can also be performed more for a long time. The terpolymer concentrate was taken out from the grinding machine, deionized water was added, and the last solid content was made 12%.

[0068] The dispersion liquid which described Prescription A were used and the ink constituent which has the following component was prepared.

Carbon black 4% (weight)

Terpolymer L 1% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water 75% [0069]

The ink constituent was prepared in the following procedure.

(1) Deionized water, PEG and 1, 3-propanediol was mixed for 20 minutes.

(2) It added into the above-mentioned mixture, stirring a terpolymer concentrate (prescription A). Stirring was continued for 20 minutes.

(3) The 20%KOH solution was added and pH of a constituent was adjusted to 8.3.

(4) It filtered by 1.2 micrometer.

[0070] This ink was used by the ink jet printer, and when it printed and examined on six typical kinds of different papers, a good maintenance property, good optical density, and the desirable advanced printing property were shown.

[0071] The ink constituent which has the following component using Prescription B and the process of a publication in the example 2 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% Polyethylene glycol (molecular weight 400) 14% 1, 3-propanediol 6% Deionized water This ink was used by the ink jet printer 76.25%, and when it printed and examined on six typical kinds of different papers, good optical density, the good maintenance property, and the desirable advanced printing property were shown.

[0072] The ink constituent which has the following component using Prescription A and the process of a publication in the example 3 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% Polyethylene glycol (molecular weight 400) 10% 1, 3-propanediol 10% Deionized water When this ink was used by the conventional ink jet printer 76.25%, the printed matter in which a good maintenance property is shown and a series of desirable advanced printing properties are shown with good optical density was obtained.

[0073] The ink constituent which has the following component using Prescription B and the process of a publication in the example 4 example 1 was prepared.

Carbon black 3% Terpolymer L 1% Brand name Liponic EG-1 10% 1, 3-propanediol 10% Deionized water When this ink was used by the conventional ink jet printer 76%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, the outstanding (good optical density is included) printing property was shown.

[0074] The ink constituent which has the following component using Prescription B and the process of a publication in the example 5 example 1 was prepared.

Carbon black 3% Terpolymer L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water When this ink was used by the ink jet printer 76.25%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0075] The ink constituent which has the following component using the process of a publication in the example 6 example 1 was prepared.

Carbon black (FW18, Degussa AG, a Ridgefield park, N.J.) 3% Terpolymer L 0.75% 1, 3-propanediol 10% Polyethylene glycol (molecular weight 400) 10% Deionized water When this ink was used by the conventional ink jet printer 76.25%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0076] The ink constituent which has the following component using the process of a publication in the example 7 example 1 was prepared.

Carbon black (FW18) 3% Terpolymer L 0.75% 1, 3-propanediol 10% Brand name Liponic EG-1 10% Brand name Kathon PFR (A destruction-of-life agent, loam & Haas) 0.15% Deionized water When this ink was used by the conventional ink jet printer 76.10%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0077] The ink constituent which has the following component using the process of a publication in the example 8 example 1 was prepared.

Carbon black (SUPESSHARUBURAKKU4A) 3% Terpolymer L 0.75% 1, 4-butanediol 10% Polyethylene glycol (molecular weight 600) 10% n-propanol 0.2% Deionized water When this ink was used by the conventional ink jet printer 75%, the good maintenance property was shown, and when it printed and examined on six kinds of typical papers, good optical density was shown.

[0078] Examples 9-11 were prepared by the same method as the example 3 explained except having used 1,5-pentanediol, 1, and 6-hexanediol and 1, and 7-heptane diol instead of examples 9-111 and 3-propanediol. When it was used by the conventional ink jet printer, the obtained ink constituent showed the good maintenance property, and when it printed and examined on six kinds of typical papers, it showed good optical density.

[Translation done.]